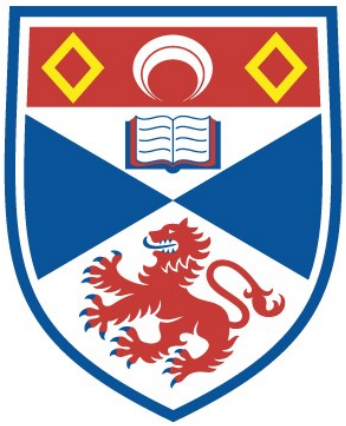
RESEARCHES ON METHYL ALCOHOL

Robert Charles Menzies

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1921

RESEARCHES ON METHYL ALCOHOL.

A Thesis presented for the Degree

of

DOCTOR OF PHILOSOPHY

of

THE UNIVERSITY OF ST ANDREWS.

By

ROBERT CHARLES MENZIES, B.Sc., A.I.C.

CERTIFICATE.

I certify that Mr R. C. Menzies, B.Sc., A.I.C., has spent nine terms at Research Work under my direction and that he has fulfilled the conditions of Ordinance No. 16 (St Andrews), and is qualified to submit the accompanying Thesis in application for the Degree of Doctor of Philosophy.

Supervisor of Research.

DECLARATION.

I hereby declare that the following Thesis is a record of the results of experiments carried out by me, and further that the Thesis is my own composition and has not previously been presented for a Higher Degree.

The research was carried out in the Chemical Research Laboratory of the University of St Andrews, under the direction of Professor J. C. Irvine.

25th June 1921.

TRAINING AND EXPERIENCE IN RESEARCH.

Educated at Merchiston Castle School, I studied Chemistry at the University of Cambridge under Dr. H. J. H. Fenton, F.R.S., from October 1905 to December 1906, and thereafter entered the University of St. Andrews in 1910. In 1916, I graduated Bachelor of Science with "Special Distinction" in Chemistry. Since 1913 I have worked in the Chemical Laboratory of the University of St. Andrews for periods broken partly by ill health and partly by the war, but amounting in all to four years.

In the summer of 1916 I acted as Lecturer to the Advanced Class in Inorganic Chemistry, but apart from this practically the whole of my time from September 1914 to July 1918 was devoted to work connected with the war conducted up to June 1916 at St. Andrews, and for the rest of the period stated, in the employment of Messrs. A. Boake Roberts & Co., Ltd., Carpenters Road, Stratford, London, E. 15. This appointment I held for three years.

Returning to St. Andrews in February 1920 I resumed a Carnegie Fellowship offered to me in 1916 but deferred owing to my holding the above war post.

LIST OF WAR RESEARCHES.

1. Research on the potash content of seaweeds for the Board of Agriculture. (September to November 1914).

2. Research on the composition of the "Green Oil" fraction of Wood Spirit for the National Health Insurance Commissioners.

LIST OF WAR PREPARATIONS.

1. Preparation of Dulcitol. (Martinmas Term, 1915).
2. Preparation of intermediate products for the synthesis of Novocain, including:-
   - a Ethylene dibromide.
   - b Glycol chlorhydrin.
   - c Diethylamino ethanol.
3. Preparation of orthoform neu.

CONTENTS.

PART I

PUTIFICATION OF METHYL ALCOHOL
BY MEANS OF
SODIUM HYPOCHLORITE.

RESEARCHES ON METHYL ALCOHOL.

While the general methods of preparing pure methyl alcohol are well known, and while the main object of the work detailed in this thesis is to describe a rapid and convenient means of removing the last trace of acetone from methyl alcohol, it is desirable, in order to define more clearly the point of departure of the work in question, to give at the outset a short account of the more common technical and laboratory processes of purification. In the course of this preliminary account it will be shown that by the ordinary methods there is little difficulty in producing methyl alcohol with an acetone content of about two per cent. For many reasons it is undesirable to alter in any essential particular the usual technical or laboratory procedure up to this stage. This residual acetone is still present in sufficient quantity to render the alcohol useless for a number of technical purposes, and its elimination by all commonly known methods is a long and tedious process involving costly operations.

The destruction of the last traces of acetone in methyl alcohol by means of sodium hypochlorite will then be described.

The general importance of the employment for synthetic work of methyl alcohol absolutely free from acetone will be emphasised. A particular instance of this will be illustrated by an account of experiments showing the changes in rotation displayed by fructose when dissolved in acid methyl alcohol containing acetone. These experiments also indicate reciprocally polarimetric tests for the presence of acetone in methyl alcohol.

THE NATURAL OCCURRENCE AND TECHNICAL PREPARATION OF METHYL ALCOHOL.

Methyl alcohol is said to occur in the fruits of certain trees, (Gutzeit, Annalen 1887, 240, 243), in meadow grass, in the leaves of chestnuts, limes, maples, and black poplar, (Lieben, Monatshefte, 1898, 19, 353), and ivy (Nicloux, Bull.Soc.Chim., 1913, (iv), 13, 939-943). The first of these papers contains merely a short recapitulation of the results of earlier work, while the second describes the products obtained on the distillation in steam of freshly gathered grass and leaves. Besides methyl alcohol the author found ethyl alcohol, formic and acetic acids, and the results are of theoretical interest. The fact, however, that from 40 kilograms of chestnut leaves, and from 60 kilograms of leaves, 7 and 10 cubic centimeters respectively were obtained makes any practical application out of the question.

Of the synthetic methods of making methyl alcohol, those starting from formaldehyde need not be discussed. Of the others, the most hopeful is probably that which consists in passing methane mixed with air or oxygen over a suitable catalyst. Modifications of this process

are the subject of two German patents. Gustav Glock (Centralblatt, 1900, II, 305) makes use of copper, and the necessary temperature according to the next quoted patent is 600°. Methyl alcohol and formaldehyde are formed. The second patent, due to the Sauerstoff Industrie Hansmann & Co (ibid., 1909, II, 1510), claims that if methane, or mixtures containing methane are passed over barks of different origin, at temperatures from 30 to 50°, methyl alcohol, formic acid and formaldehyde are formed. This observation, if true, is a remarkable one, and of both theoretical interest and practical possibilities. The idea that the surface material of plants is able to oxidise methane, as well as to reduce carbon dioxide to formaldehyde is worth attention, while the practical advantage of being able to produce at temperatures in the neighbourhood of 40° substances so easily decomposed by overheating as formaldehyde and formic acid is obvious.

While the papers and patents referred to above are instructive as drawing attention to the initial products and to the initial mechanism of the vital synthesis of vegetable matter, and while the patents may even in the future become the basis of methods for preparation of methyl alcohol, there is at the present time only one

available source of this commodity, namely the "wood spirit" obtained by the destructive distillation of lignified cellulosic material.

Now the production of pure methyl alcohol from wood spirit may be said to be one of the most vexing questions of applied chemistry.

The source and the composition of crude wood spirit supply the reason for this. The products resulting from the dry distillation of wood after removal of tar are heated with boiling milk of lime, the distillate thereafter obtained being termed crude wood spirit. This material consequently contains all those products which are not of an acid nature, and which do not enter into combination with boiling milk of lime. A list of these products given by Klar in his book on wood distillation in Germany is now given.

	Boiling point.		Boiling point.
Methyl alcohol	64.7°	Methyl ethyl ketone	79.6°
Acetone	57°	Allyl alcohol	97°
Acetaldehyde	20.8°	Furfural	159°
Dimethyl acetal	64.4°	Methyl furfural	187°
Formaldehyde	-- -	Mesityl oxide	131°
Methyl acetate	57°	Cumol	153°
Ammonia	--	Cymol	175°
Monomethylamine	6°	Pyridine	115°
Dimethylamine	7.3°	Pyrocatechin	245°
Trimethylamine	3.5	Other hydrocarbons	

To this list must be added (Mabery, American Chemical Journal, 1883, 5, 257). a small quantity of methyl formate (B.P. 30.4) and the writer can vouch for the almost certain presence of furane from his own observations that low-boiling fractions of wood spirit frequently give bright green colours with acids.

It is generally assumed that ethyl alcohol is not found in wood spirit, and while it would be a curious thing if wood spirit, containing as it does, acetaldehyde, methyl acetate, and methyl ethyl ketone, should contain no ethyl alcohol, its presence is claimed in only one paper, by Hemilian, (Ber., 1875, 8, 661). This author fractionated a product bought from Kahlbaum under the name of acetone, and obtained about a quarter of his original material as a liquid boiling from 78 to 80°. This was proved to be ethyl alcohol. The paper is dated from the Technological Institute, St Petersburg, the work having been performed in the laboratory of Professor Beilstein, who, after the above result had been obtained wrote to Messrs Kahlbaum and was informed by them that the preparation in question, in common with almost all commercial acetone, was obtained from crude wood spirit. This result obtained in 1875, and with ambiguous material is the only evidence found in the literature of the

presence of ethyl alcohol in wood spirit.

The general idea underlying the technical methods of obtaining methyl alcohol from the mixture described on page 12 is that many of the impurities present can be eliminated by alternate distillations with acid and alkali. Further, the separation of acetone, which is of all constituents the most difficult to remove, is much improved, though still imperfect, by the addition to the mixture of at least its own bulk of water. With this double object in view, Klar advises the addition to the crude wood spirit for the first distillation of 30 to 40 per cent of water and also milk of lime. In connection with this, however, the writer's experience has shown that acetaldehyde is present in sufficient amount to justify its recovery, and that the adoption of Klar's process results in the partial resinification of this product. Moreover acetaldehyde is also present in the combined form as dimethyl acetal, a compound which is quickly split up by dilute aqueous acids, yet is on the other hand stable to alkalis.

In passing it may be noted that the boiling point of dimethyl acetal is of the order 62.7 to 64.4, while that of methyl alcohol according to Sidney Young (Soc. Trans., 1902, 81, 719) is 64.7 at 760 mm. On the basis of the above observations it is probable that a preliminary

distillation over dilute aqueous sulphuric acid would increase the yield of acetaldehyde and also result in a purer nethyl alcohol being ultimately obtained.

The general effect of distilling crude wood spirit with water alone and also with the addition of alkali is illustrated below. Tables I and II, overleaf. The material in question was a dark liquid of specific gravity 0.925 and was originally sent here for examination as the product of a still which had got out of order. The sample was a typical example of very crude wood spirit containing about half its bulk of water. It was used as the source of the pure methyl alcohol afterwards described. It may be explained that the acetone was determined in each case by Messinger's method, and that any aldehydes occurring in the mixture will increase the apparent acetone value.

T A B L E I.

Distillation of 7000 cc of untreated sample. Density 0.925. (46% MeOH).
Acetone titration equivalent to 4.8% of acetone.

	B. P.	Volume	Density	Acetone equivalent	Weight as acetone	Weights from previous column added together.
Main bulk		7000 cc	0.925	4.8 %	310 gms	310 gms
F1 to	73	640 cc	0.838	8.05 %	51 "	51 "
F2 to	73.5	1085 cc	0.840	6.6 %	71 "	122 "
F3 to	75	793 cc	0.840	4.95 %	39 "	161 "
F4 to	78	973 cc	0.849	3.7 %	36 "	197 "
F5 to	79	637 cc	0.848	3.3 %	21 "	218 "
F6 to	99	918 cc	0.947	4.95 %	45 "	263 "

T A B L E II.

Distillation of 7000 cc of same sample but mixed with 350 grams of caustic soda.
Concentration of alkali = 5 per cent.

	B. P.	Volume	Density	Acetone equivalent	Weight as acetone	Weights from previous column added together.
F1	Not recorded	40 cc	0.820	9.6 %	3.8 gms	3.8 gms
F2		1264 cc	0.836	7.4 %	93.4 "	97.2 "
F3		1790 cc	0.854	1.86 %	32.3 "	129.5 "
F4		1100 cc	0.880	0.39 %	4.3 "	133.8 "
F5		970 cc	0.960	0.27 %	2.6 "	136.4 "

This second distillation which is on the ordinary lines of technical practice was accompanied by the formation of large quantities of aldehyde resin, and in technical working much aldehyde is habitually destroyed in this way. According to Klar, the first carboy collected in the large-scale distillation of wood spirit consists of 93 to 94 per cent of acetaldehyde, and while this statement seems to the writer somewhat sweeping, in the absence of express mention of brine-cooled condensers, he has himself obtained several gallons of good acetaldehyde by careful refractionation of the earlier fractions of crude wood spirit.

It will be seen from comparison of the figures quoted in Tables I and II that in the absence of alkali the total "acetone value" in the distilled fractions was 263 grams, while, by the use of caustic soda, the figure was reduced to 136 grams. This difference, as already pointed out, must be attributed to the destruction of aldehydes. An inspection, moreover, of the "acetone figures" of corresponding fractions of the two distillations indicate that acetaldehyde is not the only aldehyde present. This destruction of acetaldehyde could probably be avoided by a preliminary distillation with dilute acid, and as already pointed out on page 15 a further supply of acetaldehyde

could be liberated and recovered in this way. Of course the question of whether the acetaldehyde thus recovered could compete in cost with that now manufactured from acetylene is an economic question, which could be solved only by taking into account the local and general conditions of the industry at the time of manufacture.

Referring again to the "acetone figures" of the various fractions described in the foregoing distillations it will be noticed that the acetone tends to accumulate in the earlier fractions. In the first case, even where the evidence of the separation is vitiated by the presence of various aldehydes, it appears that the first third of the distillate contains one half of the acetone and bodies analysing as acetone. In the second place, where the aldehydes have been destroyed by alkali, the first quarter of the distillate contains more than two thirds of the acetone.

These distillations were done from a metal still through a Raschig column 34 inches high. They have been described not in any sense as anything new, but as fully bearing out the main features of Klar's description. They also illustrate, in a more concise manner than would otherwise have been possible, the general conduct of the large scale rectification of wood spirit through columns 40 or 50 feet high. The importance of alternate distillations with acid and alkali in presence of large

quantities of water has been insisted on, and the obtaining as a consequence of these operations a series of fractions with varying acetone content has been displayed.

The result of the second distillation (Table II), where the first quarter of the distillate contained two thirds of the acetone, is a perfectly general one, and may be stated thus:- If a mixture of methyl alcohol and acetone be distilled with a large bulk of water, the acetone tends to accumulate in the earlier fractions, but there is no hard and fast separation.

Any such distillation will lead to three main fractions, the first containing a greater percentage of acetone than the original material, the second about the same, and the third considerably less. This is equally the case with all concentrations of acetone ranging from 20 to 2 per cent. It follows then, that by repeating these distillations and by carefully redistilling fractions of like acetone content it is possible to reduce the acetone content of part of the alcohol to as low a figure as required.

Now, the treatments with acid and alkali also effect their purposes to greater advantage in the simultaneous presence of much water, and as the result of keeping apart fractions of similar acetone content during the course of

these necessary treatments, there is no difficulty in obtaining a considerable quantity of methyl alcohol with an acetone content of not more than two per cent.

But to obtain from this latter product methyl alcohol with an acetone content of 0.2 per cent and under, the whole of the distillations described above must be duplicated. While, consequently, methyl alcohol containing in the neighbourhood of 0.1 per cent of acetone can be and is prepared by this method, it is both slow and expensive.

The importance of the complete elimination of acetone from methyl alcohol designed for technical use may be illustrated by one example from the aniline industry; according to Klar, each kilogram of acetone present in methyl alcohol causes a loss of nearly five kilograms of aniline by condensation. The primary reaction involved probably takes the form:-

$$2\ C_6H_5NH_2 + OC(CH_3)_2 \longrightarrow (C_6H_5NH)_2C(CH_3)_2 + H_2O,$$

and. as already stated, the importance of using acetone-free methyl alcohol in synthetic organic work will be illustrated at a later stage in a description of experiments with fructose.

REMOVAL OF RESIDUAL ACETONE FROM METHYL ALCOHOL.

In view of what has been said above, innumerable methods have been suggested for the removal of the last traces of acetone from methyl alcohol. Especially during the war, when every available means of obtaining acetone had to be considered, the common feature of most of these methods was that they claimed to recover the acetone as such, and while it is established that part of the acetone can be so recovered from methyl alcohol, it is doubtful whether under ordinary conditions it is profitable to undertake this recovery from solutions with an acetone content of not more than two per cent.

The methods in question may be divided into two main groups, physical and chemical. The former, that of distillation, has already been discussed, and of the latter it will suffice to outline four, namely

(a) the calcium chloride method,

(b) the esterification method,

(c) the benzidene method, and

(d) the method of direct chlorination.

(a) The Calcium Chloride Method. This, with the esterification method, constituted the old laboratory process of purifying methyl alcohol. Thus to quote a standard description crude methyl alcohol dehydrated over lime "is mixed with powdered anhydrous calcium chloride, with which the methyl alcohol combines to form a crystalline compound of the composition $CaCl_2$, $4H_2O$. This substance is pressed between cloths or gently heated (to remove acetone), and it is then decomposed by distillation with water; the aqueous methyl alcohol is then dehydrated by repeated distillation with quicklime, but it still contains traces of acetone and other substances."

Further light is thrown on this method by a paper on Compounds of Calcium Chloride and Acetone by L. S. Bagster (Trans. Chem. Soc., 1917, 111, 494) in which it is shown that compounds of one molecule of calcium chloride with one and two molecules of acetone respectively may be isolated. Taking into account Bagster's measurements of the vapour pressures of these two compounds at various temperatures, the conclusion is inevitable that while a partial separation of acetone and methyl alcohol may be effected by this means, it must of necessity be incomplete.

(b) The Esterification Method. It is stated in the literature that pure methyl alcohol can be obtained by the preparation and subsequent hydrolysis of methyl oxalate,

but according to Grodski and Kraemer (Ber., 1874, 7, 1494) methyl alcohol obtained by this method always contains ammonia, which is best removed by further distillation over fresh methyl oxalate. Probably a better method for laboratory use is that of Klason and Norlin (Chemisches Zentralblatt, 1906, II, 1480) who recommend the use of potassium methyl sulphate. In any case, however, the cost of oxalic acid is against the first method, while both processes involve on the manufacturing scale the working up of large quantities of solid compounds, one of which is dilequesent, and is expensive.

(c) The Benzidine Method. The elimination of acetone by this method depends upon the insolubility of benzidene-acetone-bisulphite in methyl alcohol. Benzidene is dissolved in the crude methyl alcohol in amount corresponding with the acetone present. On passing sulphur dioxide through the mixture the double sulphite is precipitated and may be filtered, the acetone being thereafter recovered by distillation with sodium carbonate. While the writer believes this method to be satisfactory as regards the recovery of most of the acetone, and consequently useful under war conditions, it has the objection that the methyl alcohol left behind is contaminated with sulphur dioxide, the last traces of which are exceedingly difficult to remove.

If the methyl alcohol is required for certain contact processes the presence of traces of sulphur poisons the catalyst.

(d) The Chlorination Process. By this method the acetone is converted into chloroacetone by the direct action of chlorine, and this chloroacetone, according to Thorpe (Dictionary of Applied Chemistry, 1212, Vol.III, 478, Article on Methyl Alcohol) can be reconverted to acetone by suitable reducing agents. The methyl alcohol and the chloroacetone can readily be separated by fractionation. There are, however, two obvious objections to this method, the one being the difficulty of making stills and fractionating columns which will withstand the action of chlorine; while the other is the formation of formaldehyde, mono- and sym- dichlor methyl ether, carbon monoxide and hydrochloric acid by the action of chlorine on methyl alcohol.

It has been shown in the above that by taking advantage of the necessary initial purification of wood spirit involving distillations with acid and then with alkali in presence of water, methyl alcohol containing not more than two per cent of acetone can readily be obtained. A survey of the processes next outlined for the removal of this residual acetone leads to the conclusion that none of them

are satisfactory as technical processes, although as a laboratory means of preparing standard methyl alcohol, the use of potassium methyl sulphate may be recommended.

Since the experiments on the further purification of methyl alcohol by means of sodium hypochlorite were suggested by Messinger's method (Ber., 1888, 21, 3368) for the estimation of acetone in methyl alcohol by means of sodium hypoiodite, this method is now discussed. It is based on the well known reaction:-

$$CH_3COCH_3 + 3NaOI \rightarrow CH_3COONa + 2NaOH + HCI_3$$

and is usually carried out as follows.

A small accurately measured or weighed sample of the liquid under examination (0.1 to 5 cc. according to acetone content) is added to 25 cc. of normal caustic soda. To this is then added slowly, and with constant stirring an excess of at least 25 per cent of $\frac{N}{5}$ iodine solution. After a lapse of 15 minutes the caustic soda is neutralised, and the liquid rendered slightly acid by the addition of normal sulphuric acid, the liberated iodine being then titrated with thiosulphate solution. Each cubic centimeter of $\frac{N}{5}$ iodine solution used up indicates the presence of 0.00193 grams of acetone.

Messinger's original results were of satisfactory

accuracy, and the reliability of the method has been confirmed by Collischonn (Zeit. Anal. Chem.. 1890, 29, 563), and by its general adoption. The latter worker also showed that the sodium hypoiodite, which is the immediate product of the action between iodine and caustic soda changes rapidly into a mixture of iodide and iodate. For the success of the method it is therefore essential that the liquid to be analysed should be added with constant stirring.

Collischonn also showed that the complete formation of iodoform was not immediate, and that it is advisable to wait at least ten minutes before adding the acid. These results, even if they seem a little contradictory, are very definitely shown in a consideration of no less than 63 experiments.

Fresenius and Grunhut (Zeit. Anal. Chem., 1905, 44, 197) further point out that in an alkaline solution one molecule of sodium thiosulphate is oxidised to sulphate by four molecules of hypoiodite according to the equation:-

$$4NaOI + Na_2S_2O_3 + 2NaOH \rightarrow 2Na_2SO_4 + 4NaI + H_2O.$$

Since, moreover, on acidifying, each molecule of sodium hypoiodite thus destroyed would react with a molecule of sodium iodide with liberation of two atoms of iodine, it

follows that the titration value of an alkaline solution of iodine as estimated by standard thiosulphate is only one eighth of that in acid solution.

The writer has verified, in a qualitative manner, the truth of this statement.

Now it is a common practice in carrying out Messinger's test to add acid in amount exactly equivalent to the alkali. The remarks just quoted, considered in view of the fact that alkali is liberated in the course of the iodoform reaction ($CH_3COCH_3 + 3NaOI \rightarrow CH_3COONa + CHI_3 + 2NaOH$) indicate that this practice must introduce an error which increases with the amount of acetone present.

The practical outcome of this is that before titration with thiosulphate, acid should always be added in slight excess, and that the results of acetone estimations in which the solutions are found to be alkaline after titration with thiosulphate should be discarded.

It may be added that Fresenius and Grunhut (loc.cit.) show in a series of careful experiments that the addition of a considerable excess of acid is harmless.

The standard of accuracy obtained by this method is illustrated by the following example:- 10 cc. of acetone (density 0.8) was made up to 200 cc. with water. The solution on analysis by the method in question was estimated to contain 4.06 per cent of acetone; this is about

the same standard of accuracy shown by the results quoted in Messenger's original paper and in that of Collischonn.

The accuracy of Messenger's method is evidence that the conversion of acetone into iodoform is complete. The general similarity between iodine and chlorine compounds gave good reason to hope that acetone might be completely removed from methyl alcohol by the corresponding action of sodium hypochlorite. Sodium hypochlorite is remarkably cheap, and it has also the advantage of being much more stable than sodium hypoiodite. According to Kretzschmar (Ztschr.f.Elektrochem. 10,789,1904) (1) the reaction $3\ NaOCl \rightarrow NaClO_3 + 2NaCl$ proceeds one hundred times more slowly than the corresponding change in the case of sodium hypobromite while the velocity of this latter reaction in turn is only $\frac{1}{30,000}$ the velocity of the change of sodium hypoiodite into sodium iodide and iodate. A. Skrabal. (Sitzungsber,d.Akad.d.Wiss.Wien,math.-naturw. Kl.120, II b,Dez.1911). (1)

The necessity of preparing sodium hypoiodite in situ has already been pointed out. The greater stability of

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(1) Abegg's Handbuch der Anorganischen Chemie, Band. IV. Abteilung 2. P.305.

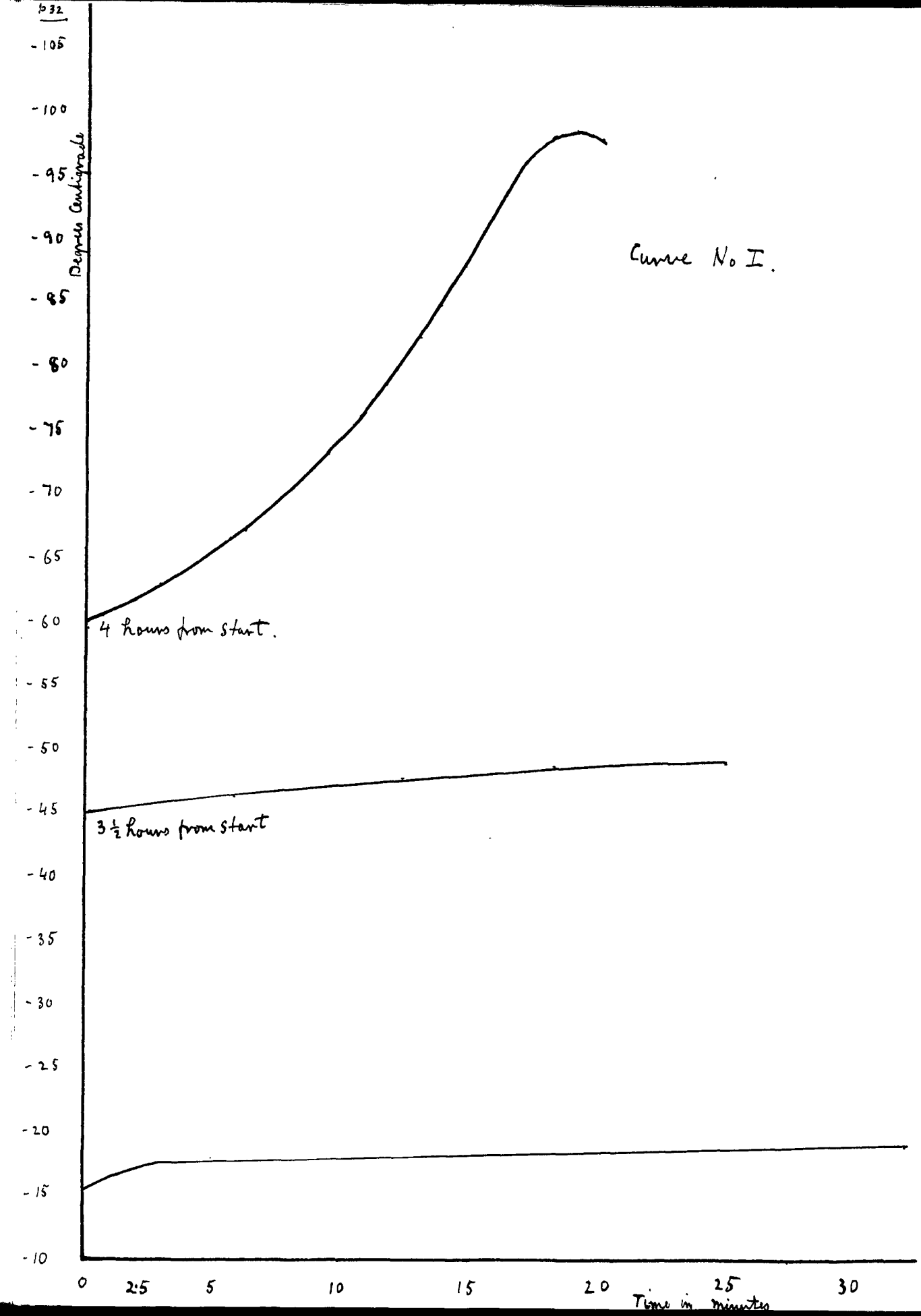
sodium hypochlorite makes it possible to adopt the more convenient course of preparing it beforehand.

Before giving an account of the purification of methyl alcohol, preliminary experiments are now described which lead clearly to the conclusions that the reaction between acetone and sodium hypochlorite begins in the cold, taking place almost instantaneously with the evolution of much heat, and that there is also at temperatures above 50° a vigorous action between methyl alcohol and sodium hypochlorite, which, however, takes place at ordinary temperatures only to a limited extent.

The conditions determining this latter reaction are quite definite and can consequently easily be avoided.

In each of the following experiments 50 cc. of a strongly alkaline sodium hypochlorite solution containing 159 grams of available chlorine per litre and 25 cc. of water were mixed with 5 cc. of the sample of alcohol under examination. The three constituents were brought to approximately the same temperature and then mixed in a Dewar's vacuum flask in which a thermometer was placed. The temperature changes observed are shown by and discussed with reference to the accompanying curves, obtained by plotting the temperatures against their respective times.

Curve No 1 shows the behaviour of the purest methyl alcohol which the writer has hitherto succeeded in making this sample had the following physical constants :-
B%P% (corr. to 760 mm.) 64.5 to 64.7°. Sidney Young (Trans. Soc., 1902, 81, 719) gives 64.7 as the boiling


-105
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-70
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-25
-20
-15
-10
Degrees Centigrade
Curve No I.
4 hours from start.
3½ hours from start
0
2·5
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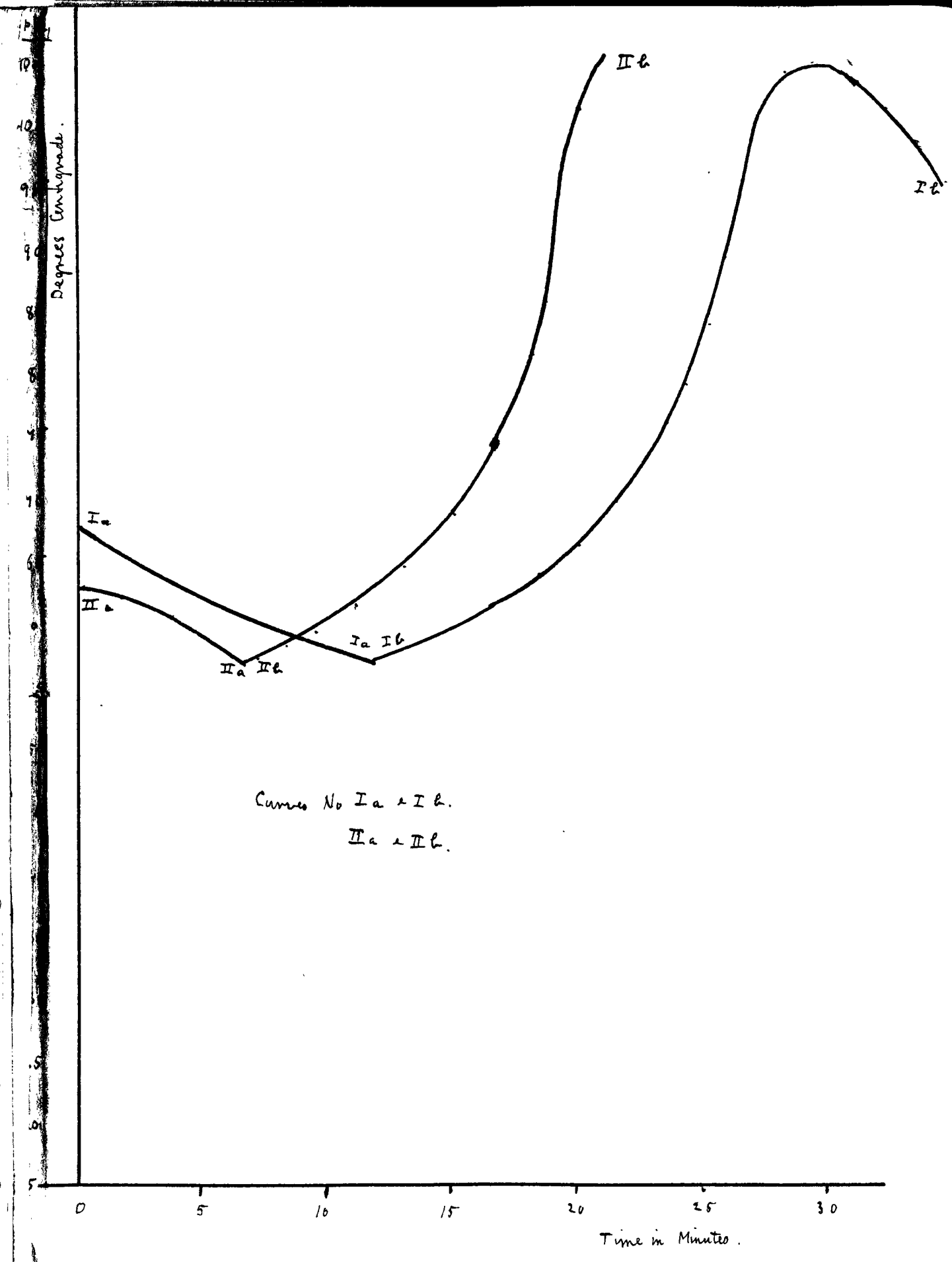
10
15
20
25
30
Time in minutes

point of pure methyl alcohol at 760 mm. The density was 0.810711 at 0°/0°. This according to Landolt's tables indicates that the sample in question contained 99.78 per cent of methyl alcohol. The acetone content was not greater than one part in 1200.

The temperature of mixing was 15° and as will be seen from the curve there was a rise of about 2.5° in the first three minutes. This was followed by a very slow rise, the temperature reaching 21.5° after 3½ hours. The mixture was then heated in an ordinary glass flask until the temperature of the liquid when poured back into the vacuum-jacketed flask was 45°. It will be seen that at this temperature there was evidence of a quicker than at 22°, there being a further rise of 4° in 25 minutes. The mixture was now again heated to 60°, and at this temperature a vigorous reaction had set in as shown by the curve which now slopes steeply upwards. The rise in temperature was only arrested at 98.5° when gentle boiling commenced.

From considerations of space, Curve No. 1 is shown in three portions, the second and third portions beginning at 3½ and at 4 hours from the start. Dotted lines occurring in other curves indicate the removal of the mixture in question from the flask and its return after warming by the application of external heat.

The curve indexed No. 1b displays the results of an experiment in which the same alcohol was used, but the

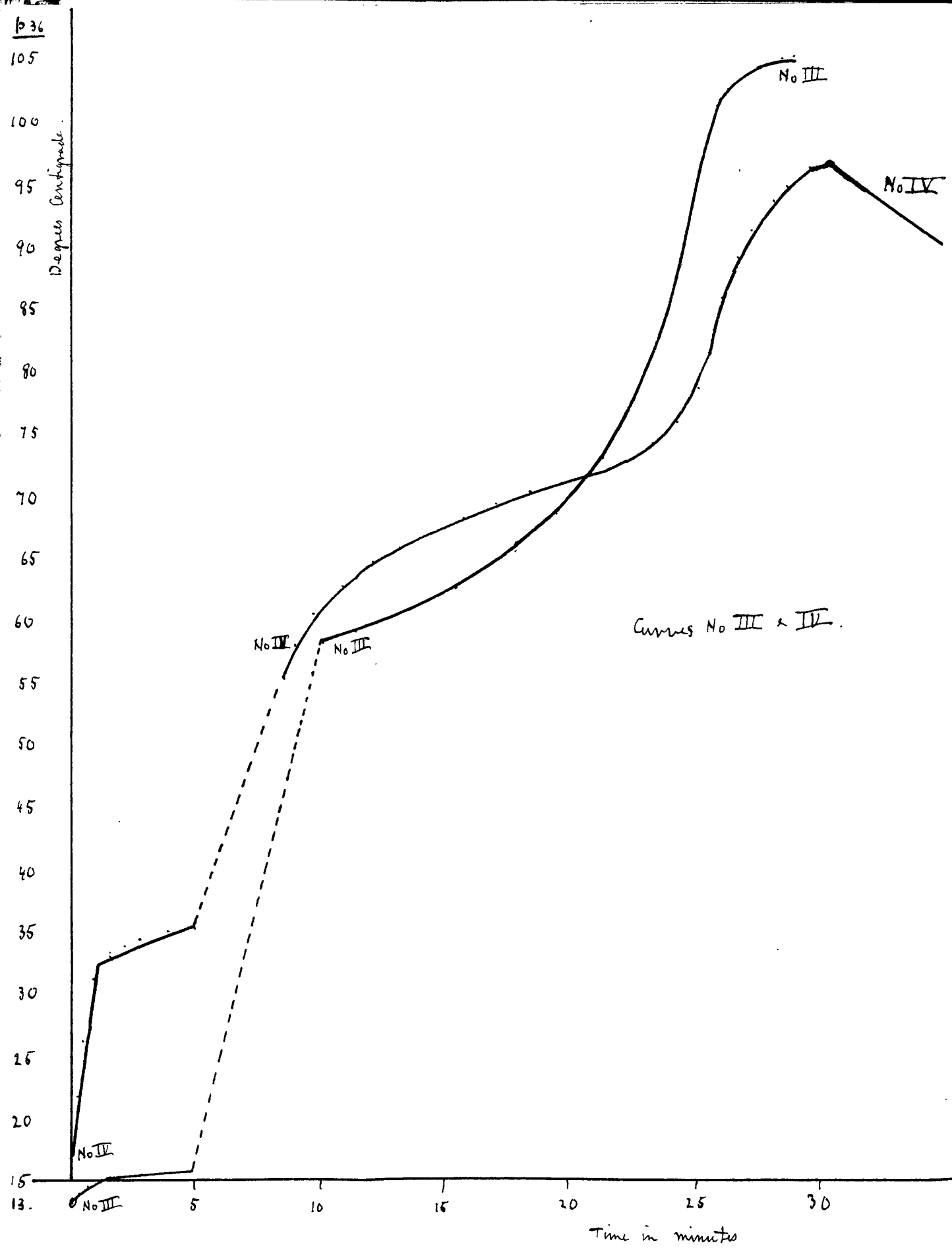


Curves No Ia & Ib.
IIa & IIb.

conditions were varied for the following reasons:- Sodium hypochlorite solutions are unstable at high temperatures, changing in heating into a mixture of chlorate and chloride. From the heats of formation of the initial and final compounds involved it is evident that the reaction should be accompanied by the evolution of a small amount of heat. (7 large calories per gram-molecular equivalent of sodium hypochlorite undergoing change).

The question consequently arose whether the shape of the curve obtained on adding alcohol to sodium hypochlorite was in any way due to this self oxidation and reduction of the hypochlorite. In experiment No.I a, the mixture of water and hypochlorite was consequently first heated to 68° without addition of alcohol; the mixture at once began to cool, the temperature falling 10° in 10 minutes. 5 cc. of the same alcohol were again added. After a preliminary cooling of 1°, owing to the alcohol having been added cold, the temperature rose rapidly as shown in I_b, a curve similar in character to, but steeper in slope than No.I. The higher gradient in this latter case is probably due to the reaction in the earlier experiment having been partially completed during the first four hours.

Curves II_a and II_b represent the results obtained in experiments duplicating those represented by curves Ia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No IV
No III
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Curves No III & IV.
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25
30
Time in minutes

13.

and Ib, with the difference that the alcohol used in experiment IIb had a boiling point 0.2 of a degree lower than that already described. Both samples of alcohol were obtained from the same distillation.

Curve No.III. displays the behaviour of Messrs May and Baker's "Pure Methyl Alcohol." This alcohol contained 0.5 per cent of acetone; its density was 0.81226 at $0°/0°$, corresponding with a purity at 99.25 per cent. It will be seen that approximately the same initial rise took place of (from 13 to 15° in this case) as in No I, and that the rest of the curve indicating the behaviour of the mixture after heating it to 55° is practically identical with No.Ia.

No.IV. illustrates a different type of reaction. The alcohol used in this case was that sold by the British Drug Houses as "Methylic Alcohol," and was found on analysis by Messinger's method to contain 11.6 per cent of acetone. The initial temperature of the 50 cc. of hypochlorite solution and 25 cc. of water was 17°; and on adding 5 cc. of this "Methylic Alcohol" (containing according to the above analysis 0.58 grams of acetone) there was a rise of temperature to 32.5°. This increase of 15.5° must be regarded as having been instantaneous, the time of one minute shown in the curve for this increase

being accounted for by thermometric lag. A further increase of 2.5° was observed in the next four minutes, after which time the mixture was heated in a flask to 55°. The curve, thereafter, while having a general resemblance to those already described, displayed the following differences:- In the first place the slope of the curve from 65 to 75° was much smaller than those of the others at corresponding temperatures; this was probably due to the distillation of chloroform formed at the commencement of the reaction. In the second place the temperature of the mixture in the present experiment never reached the boiling point of water. This in turn is probably due to the acetone having destroyed part of the hypochlorite. (A calculation shows that about 25 per cent of the hypochlorite originally present would be required to convert the acetone added with the alcohol into chloroform and sodium acetate.)

Now, as already stated, it appears from these experiments that acetone reacts instantly with hypochlorite in the cold, but that methyl alcohol reacts only at higher temperatures.

To make quite certain, however, that the initial rise in temperature shown in experiment No.IV. was due to acetone and to nothing else, a comparative experiment No.V,

not plotted, was performed. In this experiment 50 cc. of the hypochlorite solution was mixed with 28 cc. of water to which had been added 0.7 cc. (= 0.56 gram) of acetone. These proportions were adjusted so as to duplicate the acetone content and heat capacity of the sample of methyl alcohol examined above.

The temperature rose at once from 18° to 31.5°, an increase of 13.5°. This corresponds with the rise of 15.5°observed in the previous case when 0.58 grams of acetone were added with the alcohol. According to Bose (Zeit. für Phys. Chem., 1907, 58, 597) the mixture of methyl alcohol and water is always attended with the evolution of heat. It will also be recalled that in Experiments I and III initial increases of temperature of about 2° were observed. It is therefore probable that of the 15.5° increase in temperature which occurred in experiment No.IV. 2° were due to the alcohol-water heat effect, and 13.5° to the instantaneous reaction between sodium hypochlorite and acetone.

The mixture No.V. was finally heated to 54°. No further rise in temperature took place, but a slow fall was observed.

These experiments illustrate:-

1. The rise in temperature known to occur on mixing methyl alcohol and water.

2. That the reaction between hypochlorites and acetone commences instantly in the cold and takes place with considerable evolution of heat.

3. That above 50° there is a vigorous reaction between methyl alcohol and hypochlorite solution which is attended with evolution of much heat, and which does not appear to have been recorded before.

A complete discussion of this reaction is beyond the scope of the present thesis, but a review of its probable course is now given.

In the first place, further analysis of the sodium hypochlorite solution used showed that it contained 140 grams of free sodium hydroxide per litre in addition to sodium hypochlorite in quantity sufficient to set free 159 grams of free chlorine on acidification. The liquid was saturated with regard to sodium chloride, which was gradually thrown out of solution as a scum with slow simultaneous evolution of oxygen.

While the presence of a small amount of iron undoubtedly accelerated this decomposition, attention may be drawn to the statement of Muspratt and Smith

(J. Soc. Chem. Ind., 1899, 18, 210) that sodium hypochlorite is not so stable in the presence of solid sodium chloride as in its absence.

Solutions of sodium hypochlorite of this concentration are somewhat viscous, resembling in their mobility concentrated sulphuric acid. Such solutions are well known to offer strong resistence to the formation of small crystals and of small bubbles of gas, especially in the absence of suitable nuclei, and this fact may have some bearing on Katz's statement that while solutions containing equal quantities of hypochlorite and of chloride ought, from kinetic considerations, to have a strong tendency to liberate free oxygen, as a matter of fact they liberate oxygen only with extreme slowness, if at all. The reaction which then takes place is expressed by the equation

$$2NaOCl \longrightarrow 2NaCl + O_2$$

In those cases where the solution is already saturated with sodium chloride, gaseous oxygen and solid sodium chloride must be produced together; there is no doubt that the production of both will take place more readily if solid sodium chloride be already present.

Sodium hypochlorite is thus a compound containing loosely combined oxygen, readily given off with evolution of heat, and yet, owing to the viscosity of concentrated

solutions these possess the apparently contradictory property of parting with gaseous oxygen only reluctantly. The result is that sodium hypochlorite is an oxidising agent of remarkable vigour, in many respects more vigorous than hydrogen peroxide.

In writing the above the fact that sodium hypochlorite can also act as a chlorinating agent has not been overlooked. Thus to quote an example, under the influence of sodium hypochlorite bromine and iodine are partly oxidised to bromic and iodic acids, but partly chlorinated to bromine and iodine chlorides. The dual action is also very well illustrated by the action of sodium hypochlorite on acetone. In this chlorination probably proceeds simultaneously with oxidation, the reaction possibly taking the course:-

1. $CH_3COCH_3 \rightleftarrows CH_3COH{:}CH_2$

2. $CH_3COH{:}CH_2 + NaOCl \rightarrow CH_3C\begin{matrix}OH\\CH_2Cl\\ONa\end{matrix} \rightarrow CH_3COCH_2Cl + NaCH$

3. $CH_3COH{:}CHCl + NaOCl \rightarrow CH_3\begin{matrix}OH\\CHCl_2\\ONa\end{matrix} \rightarrow CH_3COCHCl_2 + NaOH$

4. $CH_3COH{:}CCl_2 + NaOCl \rightarrow CH_3\begin{matrix}OH\\CCl_3\\ONa\end{matrix} \longrightarrow CH_3COONa + CHCl_3$

In favour of this assumption is the fact, now established, that chloroacetone reacts with sodium hypochlorite instantly, the mixture boiling.

As already said this dual action of chlorination and oxidation has not been overlooked, but it is in the oxidising action of sodium hypochlorite that an explanation must be sought of its behaviour with methyl alcohol.

In the first place it may be said that the occurrence of a vigorous reaction at high temperatures with sodium hypochlorite is not confined to methyl alcohol. Ethyl alcohol behaves similarly, and the same can be said of fermentation butyl alcohol. In the latter case the mixture has to be heated almost to boiling point before any reaction begins, and as butyl alcohol is not readily soluble in water, it is necessary to stir. Once, however the mixture of sodium hypochlorite and butyl alcohol begins to boil, it continues to do so vigorously after removal of the external source of heat.

The evidence that oxidation and not chlorination accounts for the main reaction is threefold.

1. As already shown a vigorous reaction takes place between sodium hypochlorite and all three alcohols so far investigated at temperatures near the boiling point of water.

2. In the case of methyl alcohol and of ethyl alcohol no evidence of the formation of chlorinated products has been obtained.

3. In the cases of methyl alcohol and of butyl alcohol the corresponding acids were found to be present after the reaction with sodium hypochlorite.

The thermal effect of the reactions has been already discussed.

Had chlorination taken place in the case of methyl alcohol, the formation of one or other of the four chlorides of methane would have resulted. Of these, chloroform and carbon tetrachloride boil at 61.2° and 76.7°, the others boil at lower temperatures. In working practice no boiling took place below 97°. In addition, no smell suggestive of chloroform, nor of carbon tetrachloride was observed. The vapours evolved burnt with a non-luminous flame, being probably that of unchanged methyl alcohol present in excess. In the case of ethyl alcohol the vapours evolved after the same vigorous reaction also burnt with a non-luminous flame. In marked contrast, the addition of acetone to ethyl alcohol led to the formation of a luminous and smoky flame, which was tinged with green.

These observations all point to the absence of chlorinated products in the reaction between alcohol and sodium

hypochlorite. Definite evidence of the presence of formic acid was found in the reaction mixture after the reaction between methyl alcohol and sodium hypochlorite. On addition of mercuric chloride followed by cautious addition of dilute hydrochloric acid in quantity slightly more than sufficient to dissolve the precipitated mercuric oxide, the mixture on boiling gave a white precipitate. This is characteristic of formic acid. Tests performed under identical conditions on the liquids resulting from the actions between sodium hypochlorite and acetone, ethyl alcohol, and butyl alcohol all gave negative results, the corresponding mixtures prepared as above described all remaining quite transparent on boiling.

Acetic acid was not tested for in the ethyl alcohol reaction mixture, but on acidifying the butyl alcohol reaction mixture the characteristic smell of butyric acid was at once apparent to an extent which made further experiments undesirable.

The absence of evidence of the presence of formaldehyde in the case of methyl alcohol is explained by the fact that the reaction between 50 cc of the hypochlorite solution, mixed with 25 cc of water, and 4 grams of formaldehyde (i.e., 10 cc of a 40 per cent solution) was found to be only slightly less rapid than with acetone.

It also was very vigorous. Formic acid was found in the resulting liquid in considerably greater quantity than found with the same weight of methyl alcohol.

The immediate inference from this is naturally that formaldehyde is an intermediate product. But there is another consideration, the statement of which will further confirm the remark that a complete discussion of this subject is beyond the scope of the present thesis, although it affords an excellent starting point for further work.

If formaldehyde is an intermediate product in the oxidation of methyl alcohol to sodium formate by means of sodium hypochlorite, acetaldehyde should similarly be an intermediate product in the corresponding oxidation of ethyl alcohol. Now acetaldehyde is instantly and quantitatively converted by hypochlorites into chloroform and formic acid (See Utheim, Brit.Pat., 116094, 1917 for a technical application of this reaction). But as already stated neither chloroform nor formic acid could be found after the reaction between sodium hypochlorite and ethyl alcohol. This makes it improbable that acetaldehyde can be an intermediate product in the oxidation of ethyl alcohol by means of sodium hypochlorite, and also throws doubt on the intermediate formation of formaldehyde in the case of methyl alcohol.

The question, however, is an open one, and H. D. Gibbs (The Philippine J. Sci., 1912, 7, 57-74) has shown clearly that both formaldehyde and formic acid are formed in small quantities by the action of three per cent hydrogen peroxide on methyl alcohol, the presence of traces of formaldehyde being detected shortly after mixing at room temperature.

It is convenient to remark here that by no process of purification hitherto attempted has the writer succeeded in obtaining methyl alcohol which gives a zero figure by Messinger's method for estimating acetone. The lowest "acetone equivalent" yet obtained was 0.03 per cent, but it is quite possible that the sample in question did not contain any acetone, as in the analysis of this sample no iodoform was precipitated nor was there any smell of iodoform. Experiments with artificial solutions of acetone showed that under similar analytical conditions one part of acetone in seven thousand gave a cloudiness due to iodoform and the characteristic smell of this compound. The

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Kastle and Loevenhart (J.Am.Chem.Soc., 1899, 21, 262) have further shown that oxidation of methyl alcohol to formic acid by neutral hydrogen peroxide proceeds very slowly at ordinary temperatures but with great velocity at 100°, results quite comparable to those obtained by the writer.

The rapid action of alkaline hydrogen peroxide on formaldehyde with the quantitative formation of sodium formate is

conclusion is justified that in the purest methyl alcohol yet prepared in the course of this work there is some substance or substances present which reduce a small amount of sodium hypoiodite. It can now be readily understood that the possibility is by no means excluded that one of these substances is methyl alcohol itself.

That a trace of formaldehyde may also be present in purified methyl alcohol is evident from experiments quoted by Gibbs (loc.cit.) showing that methyl alcohol exposed to the joint action of air and sunlight is soon found to contain formaldehyde.

The general behaviour of methyl alcohol to oxidising agents, and its well known oxidation by air to formaldehyde in the presence of catalysts, make it quite probable that a certain amount of oxidation may take place during the distillation of methyl alcohol in the condenser in the area where the hot vapour and freshly condensed liquid come into contact with air.

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the basis of the well known reliable method for estimation of formaldehyde due to Blank and Finkenbeiner (Ber., 1899, 31, 2979).

In spite of the inconsistency referred to above these observations show that in the main the action of sodium hypochlorite on methyl alcohol is similar to that of alkaline hydrogen peroxide.

The above observations outline an interesting field of work, but sufficient has now been said to make clear the conditions which require to be complied with in the treatment of wood spirit with sodium hypochlorite to remove acetone. In the first place the temperature should not be allowed to exceed a fixed maximum, and in the second place, the hypochlorite should be added in amount only slightly in excess of that necessary to react with the acetone, as otherwise the alcohol will be attacked.

The practical application of this method is now described; this description is in two parts. In the first part, Experiments I, II & III general preliminary experiments are discussed in which attention is directed to the fact that by this method methyl alcohol can be obtained in a high degree of purity, but in which the yield of purified alcohol is not especially considered. In the second part, Experiments IV-V detailed quantitative experiments are described in which particular attention is devoted to the question of the yield. It will be shown that of every 100 grams methyl alcohol present in crude wood spirit it is possible to recover 75 grams in a pure condition.

Practical application of Sodium Hypochlorite method

Experiment I.

In a first experiment a total of 1317 cc of methyl alcohol containing 1·3 p.c. acetone obtained as described on page 15 was treated with sodium hypochlorite. The total acetone equivalent of the five portions was 17·9 grams while the total weight of methyl alcohol present (by density) was 770 grams. 395 cc of a hypochlorite solution containing 175 grams of available chlorine per litre was added, the calculated amount being 390 cc. On distillation the first fraction contained much chloroform, but the separation of this was very sharp, and after the first 100 cc the distillate no longer gave a cloudiness with water.

The remaining fractions contained 693 grams of methyl alcohol (by density), and on applying a quantitative test for acetone no separation of iodoform occurred. There appeared, however, to be traces of combined chlorine.

Experiment II.

A second experiment conducted under parallel conditions gave similar results. But in this case a longer fractionating column was used; traces of acetone

were found in the distillate, but in no case in amount greater than 0·25 p.c. After removal of the chloroform in the first 100 cc the quantity of chlorine in the distillate appeared to be small, as a sample of 25 cc taken from the next litre of distillate gave only a faint cloudiness after treatment with sodium under a reflux condensor for an hour, and addition of silver nitrate and nitric acid.

Part of the methyl alcohol purified as above described was converted into methyl acetate. This after distillation over phosphoric anhydride analysed at 99·9 p.c.

The rest of the methyl alcohol, which contained 0·25 p.c. of acetone was again treated with hypochlorite solution in considerable excess. A slow rise in the temperature was observed, greater in amount and longer in duration than could have been expected from the acetone content alone. The cause of this has already been explained. A good yield of methyl alcohol was obtained from this last treatment, the acetone content being less than 0·1 p.c. (by Messenger's Method). The density, 0·825, indicated that the alcohol was not dry; it was consequently dehydrated first over lime and then over sodium, a fraction being finally obtained having a density

of 0.7939 at 20°. The density of pure methyl alcohol is quoted in Beilstein (Loomis.Ph.Ch.32.589) as 0·79133 at 20°.

Two estimations for acetone gave 0.031 p.c. and 0·023 p.c. for this sample. 5 cc of the alcohol were taken in each case and 30 cc of $\frac{N}{5}$ iodine. The difference between the two back titrations with $\frac{N}{5}$ sodium thiosulphate was 0·2 cc, which is within the limits of experimental error. This sample of purified methyl alcohol had the lowest "acetone equivalent" of any yet obtained, and as already explained (p. 48) it is probable that no acetone was present.

The average acetone content of the initial material used for the experiments just described was 1·3 p.c., and it will be apparent that there is no difficulty in obtaining from such material methyl alcohol with a negligible acetone content by means of sodium hypochlorite. For work on the technical scale crude methyl alcohol containing up to 2 or 2½ p.c. of acetone could be conveniently purified by such means as will be shown later. The heat evolved by the action between sodium hypochlorite and acetone is so considerable that for concentrations above this latter figure it is necessary to add the sodium hypochlorite slowly with cooling. In working with large quantities the time required for one treatment would thus

be unduly prolonged.

On a laboratory scale, however, much higher concentrations of acetone can be completely removed by the use of sodium hypochlorite. As illustrating this a third experiment may be instanced.

Experiment III.

2½ litres of the earlier fractions described in tables I & II and averaging 10 p.c. acetone were treated with the same hypochlorite solution containing 175 grams of available chlorine per litre.

The hypochlorite solution was added in small quantities at a time to the alcohol fractions in large flasks, and the mixture cooled under the tap before the addition of the next portion of hypochlorite solution.

The product was distilled, and the distillate further purified as indicated below.

Table III

	"Acetone"	B.P. Corr. to 760 mm	Density 0°/0°	Per cent of MeOH by Landolt's Tables
I. Further purified over 1) H_2SO_4 ; 2) 3) over sodium	0·05%	64·5 to 64·7°	0·811076	99·67 %
II. Further purified over 1) sodium & Iodine 2). Sulphuric acid.	0·064%	64·6 to 64·9	0·811043	99·68%
III. Products of I & II mixed, then redistilled over bone char and Sodium. Middle fraction.	0·086%	64·5 to 64·7	0·810771	99·98%

% by weight

In connection with the experiments just described, a number of points may be noted. In the first place the preliminary distillation of the crude methyl alcohol over dilute sulphuric acid in presence of much water recommended on page 14 does not effect complete removal of nitrogenous bases. The sulphates of these bases appear to suffer hydrolysis in the course of distillation in the presence of water, and their complete removal can only be effected by a further distillation of the dry alcohol with acid.

Final dehydration of methyl alcohol in the laboratory is probably effected with least loss by distillation over sodium. This is naturally not applicable to technical use.

The idea has already been expressed that the small "acetone equivalents" whose analyses are unattended by the formation of solid iodoform are due to the presence of formaldehyde. Support is given to this by the fact that these small "acetone equivalents" are decreased by distillation over sulphuric acid, in one instance from 0·07 p.c. to 0·03 p.c. This is to be accounted for by the formation of methylal , which is stable to alkalis and unattacked by iodine solution.

On one or two occasions distillations were done over

sodium and iodine; this invariably leads to a product showing an increased "acetone equivalent" but yielding no solid iodoform by Messenger's test. Thus in two cases the apparent acetone increased from 0·03 p.c. to 0·06 p.c. and from 0·064 p.c. to 0·086 p.c. (See Table III) on distillation over sodium and iodine.

The most striking example of this oxidation was afforded by an experiment in which before commencing a distillation sodium hypochlorite solution was poured down the column (four feet long and filled with glass tubes cut into short lengths). The first 60 cc of distillate had an acetone equivalent of 0·39 p.c., no iodoform being formed in the analysis. The next 1350 cc had an acetone equivalent of only 0·077 p.c. All these facts are in accordance with the idea that formaldehyde is formed.

The three experiments just discussed indicate the lines along which the purification of methyl alcohol by means of sodium hypochlorite can be carried out and also prove conclusively that by this means methyl alcohol can be obtained in a high degree of purity. They were, however, of a preliminary nature and for that reason incomplete, and it is not advantageous to describe any one of them in greater detail than has already been done.

Two final purifications were now undertaken in the course of which careful note was made of points shown by the preliminary experiments to be important. These purifications are now described, attention being paid to the yield and also to the possible use of this method on the technical scale.

Experiment IV.

(a) Specification of impure methyl alcohol used.

This was sold by the British Drug Houses under the name of "Methylic Alcohol." Its density was 0·8292 at 60°, corresponding to 88·1 p.c. methyl alcohol by weight. Two analyses for acetone by Messenger's method gave 12·1 and 12·06 grams of acetone per 100 cc. The mean was taken at 12·08. The saponification value corresponded to the liquid containing 6·7 grams of methyl acetate per 100 cc.

From these figures, making allowance for the methyl acetate and for the acetone present, it follows that not more than 576 grams of methyl alcohol can be present per litre of "Methylic Alcohol."

(b) Particulars of sodium hypochlorite used.

One kilogram of Crossfield's "98–99 p.c. Pure Powdered Caustic Soda" was dissolved in 4 litres of water.

After cooling, 680 grams of chlorine (by direct weighing) were then passed into this solution with external cooling, this being 78·5 p.c. of the amount of chlorine theoretically required for total conversion to hypochlorite.

Two analyses of the solution of sodium hypochlorite thus obtained gave 144·2 and 145·2 gms of available chlorine per litre. The mean is 144·7.

Now, as already stated, 1 gm. molecular weight of acetone (58·06 gms.) requires theoretically six atomic equivalents of chlorine, and from this it can be calculated that 25·32 cc of this solution are required to convert 1 gram of acetone into sodium acetate and chloroform.

(c) Details of Experiment. IV

One litre of the "Methylic Alcohol" was mixed with two litres of water, thus giving a mixture with an acetone content of 4.03 p.c. This consequently contained 120·8 grams of acetone, and should therefore require 3059 cc of the hypochlorite solution described under (b) above.

With the object of testing the exactitude of the method a slight deficiency of sodium hypochlorite, namely 2800 cc, was first added. This theoretically should remove $\frac{2800}{25.32}$ = 110·6 grams of acetone, and there should be left 10·2 grams of acetone.

After adding the hypochlorite solution the chloroform produced settled to the bottom on standing. The clear brown supernatant liquor was syphoned off as completely as possible, and the chloroform separated from the remainder in a separating funnel. The top layer had now a volume of 5700 cc while that of the chloroform layer was 103 cc (weight 145 gms).

The main bulk of the solution, the "brown supernatant liquor" already referred to, was analysed for acetone; found 0·106 p.c. and 0·097 p.c., mean 0·1015 p.c. This result indicated the presence of 5·77 grams of acetone in the layer in question. As this was little more than half of the acetone expected, the acetone constant of the chloroform layer was then determined and found to be 3·5 p.c. corresponding to 3·6 grams in 103 cc. In both these analyses solid iodoform was formed.

Thus of the 10 grams of acetone left unacted on, 9·37 have been accounted for, and the acetone content of the aqueous alcohol mixture was as stated reduced to 0·1015 p.c.

Removal of this residual acetone.

To 5500 cc of the solution from the experiment just described, and containing in all 5·58 gms. of acetone, 255 cc of the hypochlorite solution were added (sufficient to destroy 10·07 gms. of acetone).

Now if the reaction is quantitative 5·58 × 25·32 cc = 141·3 cc of the hypochlorite solution should be used up by the acetone, and there should be an excess of 113·7 cc of hypochlorite. Provided this does not enter into any extraneous reaction there should now be 113·7 × 0·1447 = 16·45 grams of available chlorine in the whole liquor.

This addition of 255 cc of sodium hypochlorite was made on 22/4/21 and the following table shows the available chlorine and "acetone equivalents" found on the three succeeding days. It may be said that in no case was any cloudiness due to iodoform noticed.

It is remarkable that the addition of sodium hypochlorite in excess of that sufficient to remove the last traces of acetone was attended by the discharge of the brown colour.

T A B L E I V .

Date.	Acetone equivalent" p.c.	Free Chlorine p.c.	Total Free Chlorine in 5755 cc.
22/4/21	------	----	16·45 gms. (cal.)
23/4/21	0·024	0·064	3·7 gms.
24/4/21	0·04 No iodoform.	0·027	1·6 gms.
25/4/21	0·03	0·005.	0·3 gms.

These results show conclusively that the removal of acetone from methyl alcohol by means of sodium hypochlorite proceeds quantitatively, one gram molecule of acetone requiring six atomic proportions of chlorine.

Table IV also indicates that any excess of sodium hypochlorite is slowly destroyed.

Recovery of pure methyl alcohol from above aqueous solution.

This aqueous solution of methyl alcohol (now 5630 cc) was distilled from a metal still through a Raschig column four feet high, the distillation being discontinued when the thermometer at the head of the column registered 100°.

The following fractions were obtained.

Table V

No.	Temperature.	Volume	Weight	Density.	Refractive Index.	Acetone %.	Total Chlorine %
F_1	64 to 64°	50 cc	45·9 gms	0·918	1·3437	0·14	0·13
F_2	67 to 77°	75 cc	62·8 gms	0·837	1·3437	0·11	0·09?
F_3	77 to 78·6°	100 cc	85·1 gms	0·851	1·3440	0·085	0·005
F_4	78·6 to 80·4°	200 cc	172·1 gms	0·8605	1·3444	{0·058 / 0·068}	0·0007
F_5	80·4 to 92°	200 cc	175 gms	0·875	1·3456	0·055	0·002
F_6	92 to 98°	500 cc	480·1 gms	0·960	not taken	0·0155	not taken
F_7	98 to 100°	500 cc	494·7 gms	0·989	not taken	0·008	0·0035.

With regard to this table it may be said that in the analysis of fraction 1. a cloudiness due to acetone was noticed; this cloudiness grew fainter with each successive fraction, and was just perceptible in the case of F4.

The estimations of chlorine were carried out as follows: 5 grams of sodium were dissolved in 100 cc of absolute ethyl alcohol, 5 cc of the fraction under examination was introduced and the mixture boiled for 1½ to 2 hours under a reflux condensor. Water was then added, and the chloride present was estimated by means of titration with $\frac{N}{10}$ silver nitrate and $\frac{N}{10}$ ammonium thiosulphate solutions after acidification with nitric acid. A blank experiment showed that any correction necessary for the chlorine in the reagents used was negligible.

With the further intention of estimating the accuracy of the method, 0·398 grams of chloroform (containing 0·354 gms. of chlorine) were dissolved in 250 cc of dilute ethyl alcohol, thus giving a solution containing 0·1416 p.c. of combined chlorine.

An analysis by the above method and employing 10 cc of the solution gave as a result 0·115 p.c. The results in the last column of Table V. must therefore be considered as

comparative rather than as absolute, especially when it is taken into consideration that F 3 giving ·005 p.c. of chlorine required only 0·07 cc of $\frac{N}{10}$ silver nitrate, and the others in proportion.

The last two fractions F6 and F7 described in Table IV were now redistilled through a column up to 98°. The distillate thus obtained and the other five fractions were then mixed, there being obtained 920 cc in all, with a density of 0·895 at 18°. This corresponds to approximately 60 p.c. alcohol by weight, and indicates the presence of 483 grams of alcohol instead of 576 calculated below as the total originally present in the one litre of "Methylic Alcohol" taken.

This alcohol was now dried by distillation over sulphuric acid and finally over sodium; as already indicated the use of sodium affords a rapid and convenient laboratory method of drying alcohol.

The fractions finally obtained are shown below.

Table VI

Final distillation of methyl alcohol obtained by purification of 1000 cc of the British Drug Houses "Methylic Alcohol"

No	Temperature	Weight	Density (15·5°)	Refractive Index	Acetone %	Total Chlorine %
F_1	63 to 65·6°	39·9 gms	0·798	1·3351	0·04	0·003
F_2	65·6 to 66·4°	375·1 gms	0·8008	1·3357	0·063	0·0036
F_3	66 to 70°	41·9 gms	0·081	1·3378	0·15	not taken.

From Landolt tables, F_1 contains 99·25% Methyl Alcohol or 39·7 gms
F_2 contains 98·3% Methyl Alcohol or 368·6 gms
F_3 contains 95 % Methyl Alcohol or 39·8 gms
A total of 448·1 gms

As already explained not more than 576 grams of methyl alcohol could have been present in the litre of "methylic alcohol" originally taken so that this recovery of 448ngrams is 76 p.c. of the maximum.

Experiment V.

This experiment was conducted in much the same manner as Experiment IV, and need not be described in detail.

In this case 500 cc of another sample of commercial methyl alcohol was taken, this was found on analysis to contain 7·9 gms. of acetone per 100 cc and not more than 79·3 p.c. of methyl alcohol by weight.

After treatment similar to that just described, except that in the final dehydration use was made of quick lime, the following fractions were obtained on distillation.

TABLE VII

No.	Temp.	Weight.	Density	Acetone p.c.	Chlorine p.c.
1.	66·5 069	203 gms.	0·82235 (0°)	0·116 (No iodoform).	0·0114 p.c.
2.	69 072	57 gms.	0·824 (15·5°).	0·2 p.c. (Trace iodoform)	0·0085 p.c.

From Landolt's Tables:-

F 1 contains 95·6 p.c. methyl alcohol by weight or 194 gms.
F 2 contains 90 p.c. methyl alcohol by weight or 51 gms.

A total of ..... 245 gms.

This is 59·4 p.c. of the weight of the crude alcohol taken and the yield is consequently 74·9 p.c.

The higher acetone figure and the trace of iodoform found on analysis of the second fraction is probably due to the formation of a small quantity of calcium acetate from the methyl acetate originally present in the raw material used for this experiment to the extent of 1·04 grams in 100 cc. This on the strong heating necessary to drive over the last fraction of the alcohol from the lime was bound to yield a little acetone.

Heat effect of the chlorination of acetone.

One more point now remains, namely an account of the heat evolved during the addition of sodium hypochlorite to methyl alcohol acetone mixtures. It may be explained that this account is not a detailed thermal study of the reaction. It is intended merely to serve as a guide for repetition of the work on a larger scale, and to give

an indication of concentrations of acetone and of sodium hypochlorite which can conveniently be used.

In the course of Experiment IV careful record was kept of the heat liberated, but to avoid obscuring the main issues - the purity and the yield of the methyl alcohol recovered - its discussion has been deferred.

It will be recalled that in Experiment IV one litre of "Methylic Alcohol" containing 12·08 grams of acetone in 100 cc was mixed with two litres of water, thus giving three litres of a solution containing 4·03 p.c. of acetone, and that to this was added in the first instance 2800 cc of sodium hypochlorite containing 144·7 grams of available chlorine per litre.

This quantity of sodium hypochlorite was added in smaller measured amounts and the rise of temperature due to each addition noted.

The initial temperature of the sodium hypochlorite solution was 15° while that of the diluted alcoholic solution was 19°.

T A B L E V I I .

Added to 3 litres of the above alcohol (originally at 19°).

(a) 300 cc sodium hypochlorite sol^{n}. 144·7 gms. per litre
temperature rose to 28°.

(b) 330 cc sodium hypochlorite sol^{n}. 144·7 gms. per litre
temperature rose to 36°.

(c) 370 cc sodium hypochlorite sol^{n}. 144·7 gms. per litre
temperature rose to 43°.

Total rise for first 1000 cc
hypochlorite $\begin{matrix}43\\19\end{matrix}$ ..... 24°.

The solution was then cooled to 24° and

(d) 1000 cc sodium hypochlorite solution were then added.

Temperature rose to 42°.

Rise for second 1000 cc
hypochlorite $\begin{matrix}42\\24\end{matrix}$ ..... 18°

The solution was again cooled to 18° and

(e) 800 cc sodium hypochlorite solution finally added.

Temperature rose to 28·5
Rise for final 800 cc
hypochlorite $\begin{matrix}28.5\\18\end{matrix}$ ..... 10·5°.

Total rise for addition of 2800 cc
hypochlorite solution 24+18+10·5 = 52·5°.

This rise in temperature is too great to be suitable for a large scale process, and indicates that other things being similar the acetone content of wood spirit to be treated in large scale work ought not to exceed 2·5 to 3 p.c.

In Experiment V the alcohol was diluted with water to an acetone content of 2 p.c.

Exact measurements were not taken, but the necessary amount of sodium hypochlorite was added at one operation and the temperature was not inconveniently high.

In the foregoing pages a method of removing acetone from crude methyl alcohol by means of sodium hypochlorite has been described. It has been shown that as a laboratory method it is satisfactory, methyl alcohol of satisfactory purity being obtained easily and in good yield.

Since sodium hypochlorite is a liquid and since it does not attack iron, this method possesses advantages over those making use of calcium hypochlorite and of free chlorine.

P A R T II.

A STUDY OF THE CONDENSATION

OF

FRUCTOSE WITH METHYL ALCOHOL.

In Part I. a detailed account has been given of a method by which methyl alcohol of a high degree of purity can readily be prepared. Equally pure methyl alcohol has without doubt been prepared in the past, but usually in the course of accurate determinations of the physical properties of this compound. The organic chemist, however, has frequently been content to accept as pure a product sold as pure by the dealers, and there is no certainty that research work involving the use of methyl alcohol has hitherto been systematically carried out with material shown to be free from acetone and from water, and agreeing closely in its physical properties with those of the pure substance.

Such material, being now available, has been used in the experiments about to be described on the behaviour of fructose dissolved in acid methyl alcohol. It will be shown that information has been obtained and forecasts verified in a manner impossible with the less pure material hitherto employed.

A discussion of the work presents difficulties, as the results are manifold. There is not one story to relate, but several. They are interwoven, and the clear presentation of each as the arguments cross

and recross is not easy, and quite impossible without a certain amount of repetition.

It is therefore convenient to summarise the results of previous work on methylfructoside, and then to discuss again each point in the light of the results of experiments with methyl alcohol, both pure and containing known amounts of acetone or water. These experiments are described in detail in Part III.

Methyl fructoside was first prepared by Fischer (Ber.1895,28,1160). Fructose was dissolved in nine times its weight of dry methyl alcohol, and a solution of hydrogen chloride in methyl alcohol was then added, so that the acid concentration became 0·5 p.c. Fischer states, without giving any analytical details, that after 48 hours at 35°, 8 p.c. of the sugar was unchanged, the remainder being converted into methylfructoside.

Further study of this compound was undertaken by Purdie and Paul (Soc.Trans.1907; 91;289), using alcohol which in the opinion of Irvine and Robertson (ibid.1916; 109, 1305) must have contained about 0·7 p.c. of acetone, (and in the opinion of the present writer, probably water as well).

Purdie and Paul obtained a laevorotatory syrup by following Fischer's directions, except that instead

of heating to 35° for 48 hours, they kept their solutions for 200 hours at room temperature before neutralising. No analysis of this syrup is given, but strong evidence as to its composition - in part, at any rate, is given by the fact that on methylation a compound was isolated which gave analytical figures agreeing well with those required by tetramethylmethyl-fructoside. The yield of this latter compound was poor (19 grams from 60).

From the standpoint of the present discussion, however, a more important ~~point~~ part of their work was their study of the optical changes occurring during the course of the condensation of the sugar with the alcohol.

Four minutes after adding the hydrogen chloride (0·5 p.c.) to a 10 p.c. solution of fructose in methyl alcohol, the observed laevorotation recorded by Purdie and Paul (2dm. tube at room temperature) was - 11·92. Four hours after mixing this had risen to* - 0·99, this being the maximum. A slow fall was then observed, the

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* As alterations in sign were frequently encountered in the course of the present work all relative optical changes are expressed algebraically. The change - 11·9 → - 0·99 is thus referred to as a rise.

original value of about - 12 being again reached after 200 hours.

After this lapse of time the solution was neutralised, the solvent removed by evaporation, and the resultant syrup used for the preparation of the tetramethylmethylfructoside already mentioned.

It is noteworthy that in their discussion of results Purdie and Paul call attention to the possible formation of a dextrorotatory methylfructoside, and this point is again raised by Messrs. Haworth and Law (Soc.Trans.1916,109,1325).

Nine years later this work was repeated by Irvine and Robertson (Loc.citl), who describe two experiments.

In the first experiment they took 15 grams of fructose, dissolved in 135 cc of methyl alcohol containing 5 p.c. of acetone. The change of rotation was observed, and the action arrested with silver carbonate when this had reached a maximum (4 hours). After removal of the alcohol under diminished pressure, the syrup was extracted with ethyl acetate, and 1 gram of a viscous clear liquid having the composition of a methylfructosidemonoacetone was obtained. This is a yield of 6.7 p.c.

In the second experiment they took 35 grams of fructose in 315 cc of methyl alcohol (1 gram of fructose to

9 cc of methyl alcohol in each case), but deferred neutralisation until the rotation had again become constant (i.e., for 200 hours).

In this case, by the same treatment, 4·3 grams of the same methylfructosidemonoacetone were obtained, a yield in this case of 12·3 p.c.

These figures indicate that at the maximum rotation the condensation with acetone is not so complete as at the later stage when the original laevorotation is again observed. Confirmation of this idea will be found below.

Irvine and Robertson attribute the initial rise in rotation to the presence of acetone, and state that the methyl alcohol recovered from the above condensation no longer exhibits this preliminary rise when used as solvent for an acid fructose solution. This changed behaviour they attribute to the removal of acetone by condensation with fructose.

Results described later are in direct contradiction to this, but a possible explanation is that their recovered alcohol must have contained water resulting from the condensation of fructose with both alcohol and acetone, and it is now found that water has a marked influence on the changes in rotation.

One important point discovered by Irvine and

Robertson is that a form of methylfructoside possesses an extraordinary capacity to condense with acetone and this reaction is the basis of a process for removing acetone from methyl alcohol.

The main point brought out by the authors cited above are now seen to be.

1. Methylfructoside is formed by the action of acid methyl alcohol on fructose, after 48 hours at 35°, or after 200 hours at room temperature. The composition of the compound is based on its conversion into tetramethylmethylfructoside, by the action of silver oxide and methyl iodide. The yield however is poor.

2. Evidence by Purdie and Paul pointing to the existence of a dextrorotatory methylfructoside. This compound, however, has not hitherto been isolated.

3. The demonstration by Irvine and Robertson that the methyl alcohol used by Purdie and Paul must have contained acetone, and that in its presence methylfructoside is not the only product, methylfructosidemonoacetone being formed as well.

4. The use of this condensation by its discoverers as the basis of a process for removing acetone from methyl alcohol.

1. Of the four points outlined on the previous page, the first is an accomplished fact and requires no further comment. The remaining three are now discussed with reference to the work detailed in the experimental part.

2. A dextrorotatory methylfructoside.

The preparation of a dextrorotatory methyl-fructoside in good yield and in the short space of 40 minutes is an interesting definite result now obtained for the first time by the use of pure dry methyl alcohol.

Its undoubted formation is made evident by an inspection of the record of the experiment indexed as Fructose Experiment V (Part III, p 107 below).

In this Experiment a 2½ p.c. solution of fructose was made up with methyl alcohol containing 0·5 p.c. of hydrogen chloride. The solvent alcohol had been freed from acetone by the hypochlorite method and from water by distillation over sodium immediately before use.

The rotation of such a mixture at 20° changes sign in about 12 minutes after mixing, and reaches a maximum positive rotation in less than half an hour.

The action was arrested after 40 minutes by the addition of a solution of sodium in the same dry alcohol, this being added until the solution was just alkaline to litmus.

This solution was allowed to evaporate slowly in a dessicator over sulphuric acid. Thirty days thereafter a portion of the resulting syrup, still alkaline, but almost colourless, was redissolved in alcohol and found to be still dextrorotatory.

A combustion of the syrup gave C = 42.83 p.c., H = 75 p.c. and a zeisel OCH_3 = 15.94 p.c. (the latter result owing to an accident in manipulation is a little low).

Methyl fructoside $C_6H_{11}O_5 \cdot OCH_3$ requires C= 43·3 p.c.; H = 7·2 p.c. OCH_3 = 15·89 p.c., while fructose $C_6H_{12}O_6$ requires C = 40 p.c.; H = 6·7 p.c.

The carbon figure, and the fact that the syrup still reduced Fehling's solution indicate that fructose or other reducing impurity was present as well. The percentage of hydrogen, moreover, might indicate contamination with water or with methyl alcohol, but the presence of either is difficult to understand in view of the syrup having been dried for 3 hours at 50° to 65°/10 mm., and later for 2 hours at 75°/10 mm.

This latter temperature appeared in no way to decompose the syrup, but it lost nearly 2 p.c. in weight. Subsequent heating for 1½ hours to 50 to 60°/10 mm. left the weight unchanged.

It may be mentioned that Fischer (loc.cit.) gives figures agreeing closely with the theoretical values for a

methyl sorboside dried in vacuo at 70°.

These analyses, afford strong evidence that the larger part of the fructose originally present had been converted into a dextrorotatory methylfructoside.

The results of the experiment indexed as Fructose Experiment IV (Part III, p104) in which a 10 p.c. solution of fructose was used also point in the same direction, although in this case, the rotation did not change sign. The observed maximum, however, in a 1 dm. tube indicates that at this point the specific laevorotation was less than one fifth of the corresponding laevorotation deduced from Purdie and Paul's observed maximum.

In this case the reaction was arrested about an hour after the minimum had been reached, i.e., about 90 minutes from the start.

Here again the carbon content (41·89 p.c.) was low, while the hydrogen (7·41 p.c.) was high.

Two separate determinations of the methoxy content gave 16·15 p.c. and 16·17 p.c.

The syrup in the second case was first dried for a period of 16 hours at 60°/ 160 mm., after which further heating for two hours to 60°/10 mm. caused no further loss of weight.

This syrup also reduced Fehling's solution.

Both syrups decolourised permanganate solution, not instantaneously, but after about two minutes, resembling in this respect the dextrorotatory oil assumed by Haworth and Law (Loc.cit. p.1325) to be a tetramethyl-methylfructoside.

Investigation of these syrups has not been carried further, as the present work concerns the properties of pure methyl alcohol rather than those of fructose, and enough has now been said to indicate that by the use of pure dry methyl alcohol a good yield of a dextrorotatory methylfructoside can be obtained in 40 minutes. This substance is of obvious importance in the consitutional study of the sugars and has not hitherto been prepared.

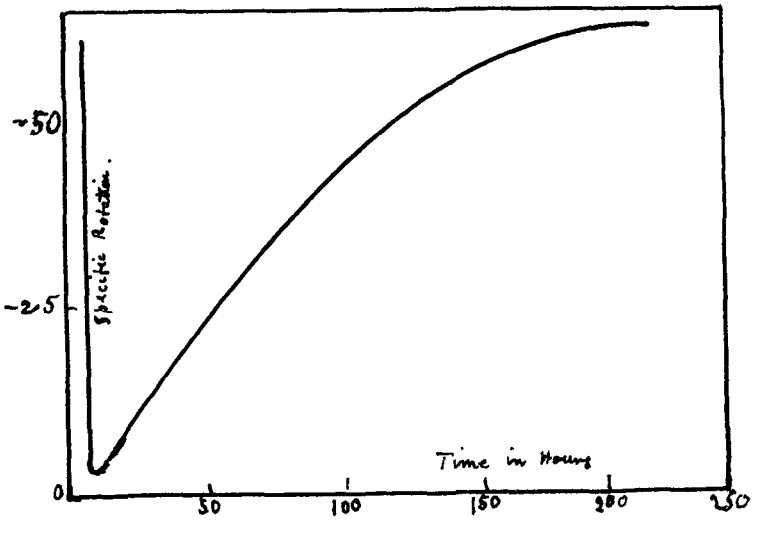
Investigation of the remaining points 3 and 4 involves the presentation and discussion of a number of curves obtained by the plotting of polarimetric readings against time. An explanatory account of these curves is given first.

In the different experiments which are illustrated three different percentages of fructose were employed, 2½ p.c., 5 p.c., and 10 p.c. In each case the observed polarimetric readings have been converted into specific rotations.

The intention was to use throughout a solution of hydrogen chloride in methyl alcohol containing 0·5 p.c. of acid, but it was subsequently noticed that the stock

solution (5 p.c. H Cl) used became weaker in a regular manner with the lapse of time owing to the formation of methyl chloride. Thus on 4/5/21 it was 5·4 p.c.; on 21/5/21 it contained 4·96 p.c., while on 8/6/21 only 4.5 p.c. Consequently in all experiments performed between the above dates the exact percentages of hydrogen chloride added has been estimated by interpolation from the curve made by plotting these percentages against the dates. The said curve is nearly a straight line.

Finally it will be recalled that the readings taken by Messrs. Purdie and Paul extended over a period of 200 hours, (the curve obtained by them traced from that given in their paper, being shown below). The curves obtained in the present work all bear a general similarity to that of Purdie and Paul if the same time scale be employed.



The main differences noted all occur during the first four hours, and within that short initial period are very significant. Beyond that time differences do exist, but they are small and irregular, and may reasonably be accounted for by small differences in the acid concentration and by differences of temperature.*

Points 3 and 4 (p. 75) raise the question of the influence of acetone on the changes taking place in an acid solution of fructose in methyl alcohol.

Influence of water on condensation between Fructose and Methyl Alcohol.

Now whether fructose condenses with methyl alcohol or with acetone, and *a fortiori* when it condenses with both at once, water is eliminated. It is natural to suppose therefore that the more water present, the less condensation can take place, and since this condensation has been proved

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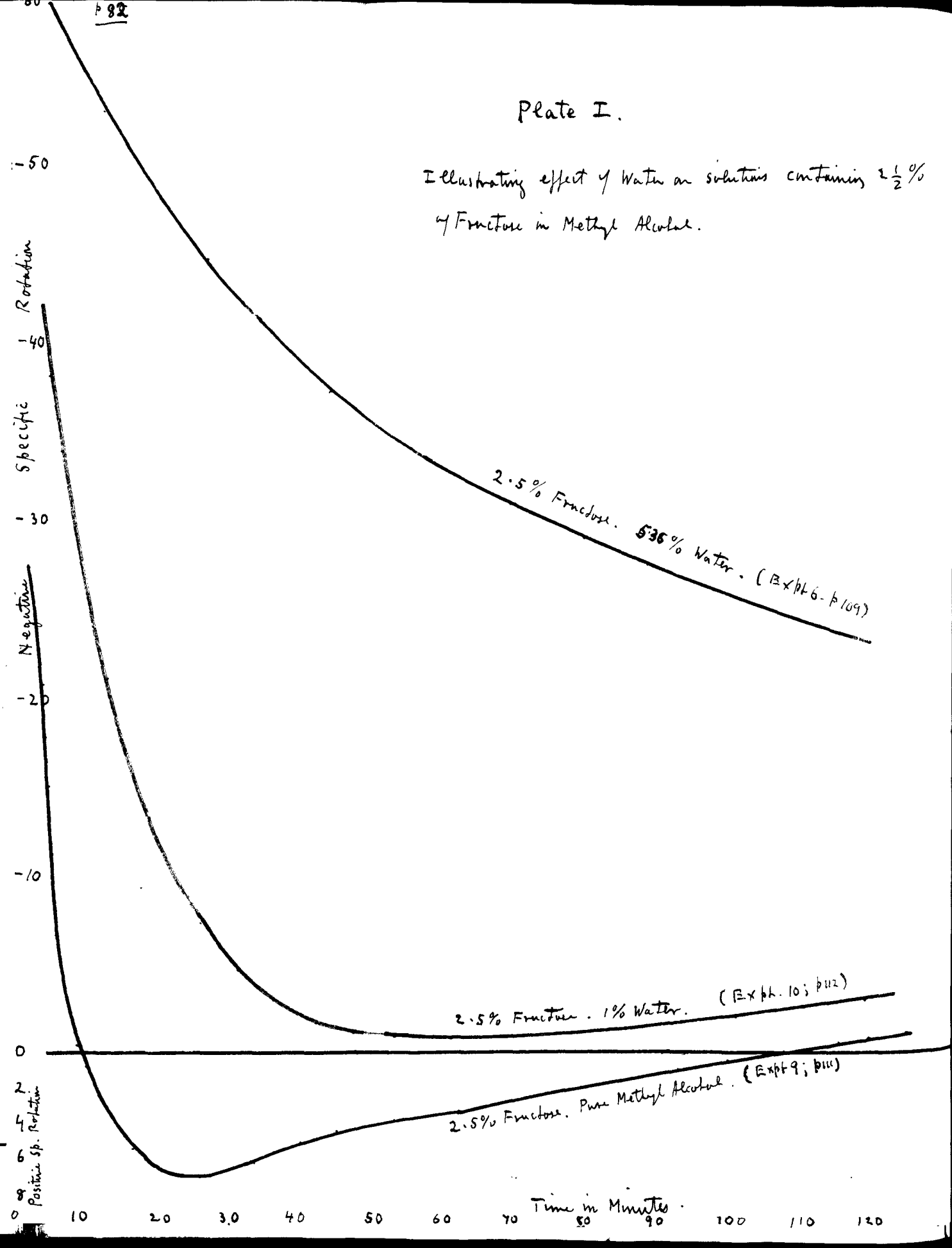
* The experimental work bearing on the above statements in the text was conducted during the coal strike and owing to the consequent stoppage of the gas and electrical supplies from 6 P.M. to 6 A.M., it was impossible to employ a thermostat for more than a few hours at a time.
The comparison of curves, is consequently confined to those denoting the changes during at most the first four hours of the various experiments.

Plate I.

Illustrating effect of Water on solutions containing 2½% of Fructose in Methyl Alcohol.



above to lead in the first instance to the formation of a dextrorotating body, it also follows that the more water present, the less will be the initial tendency for the solution to become dextrorotatory. . In other words, the greater the proportion of water present the flatter should be the curve.

That this is the case is shown by the accompanying blue curves (Plate I) illustrating the effect of 1 p.c. and 6·5 p.c. of water on a 2½ p.c. solution of fructose in acid methyl alcohol. The black curve shows the changes occurring when dry alcohol is used. It will be seen that the presence of as little as one gram of water in 100 cc inhibits the change of sign.

It may be said at once that this effect of water in flattening the curve possibly offers an explanation of Irvine and Robertson's statement (Loc.cit.1310) that on repeating an experiment with methyl alcohol recovered from a previous experiment, the preliminary rise in rotation does not take place.

This, as already stated, is in direct conflict with the writer's result, who found the two curves to be practically identical (Plate III).

It has to be pointed out, however, that Irvine and Robertson arrested the reaction by means of silver carbonate. Their recovered alcohol must consequently have contained

more water than the alcohol with which they commenced. The effect of water in inhibiting the preliminary rise has now been described.

The present experiments, on the other hand, were all arrested by the use of sodium dissolved in dry methyl alcohol, with the result that the recovered alcohol also was dry as may be seen by comparison of the boiling points and densities. (Experiment I. p. 97 and p. 100).

The use of sodium methoxide is a great saving of time. It was employed, partly for this reason, partly as stated to recover dry methyl alcohol, and partly also because the possible formation of γ fructose derivatives was under consideration. These compounds are very susceptible to oxidation and silver oxide and carbonate as oxidising agents are best avoided.

Its use, however, is not without the disadvantage that the resulting sodium chloride is appreciably soluble in methyl alcohol, and apparently in methyl fructoside as well. As a result, the syrup obtained from Experiment IV. contained 6·2 p.c. of ash, and that from Experiment V. 6·99 p.c.[x]

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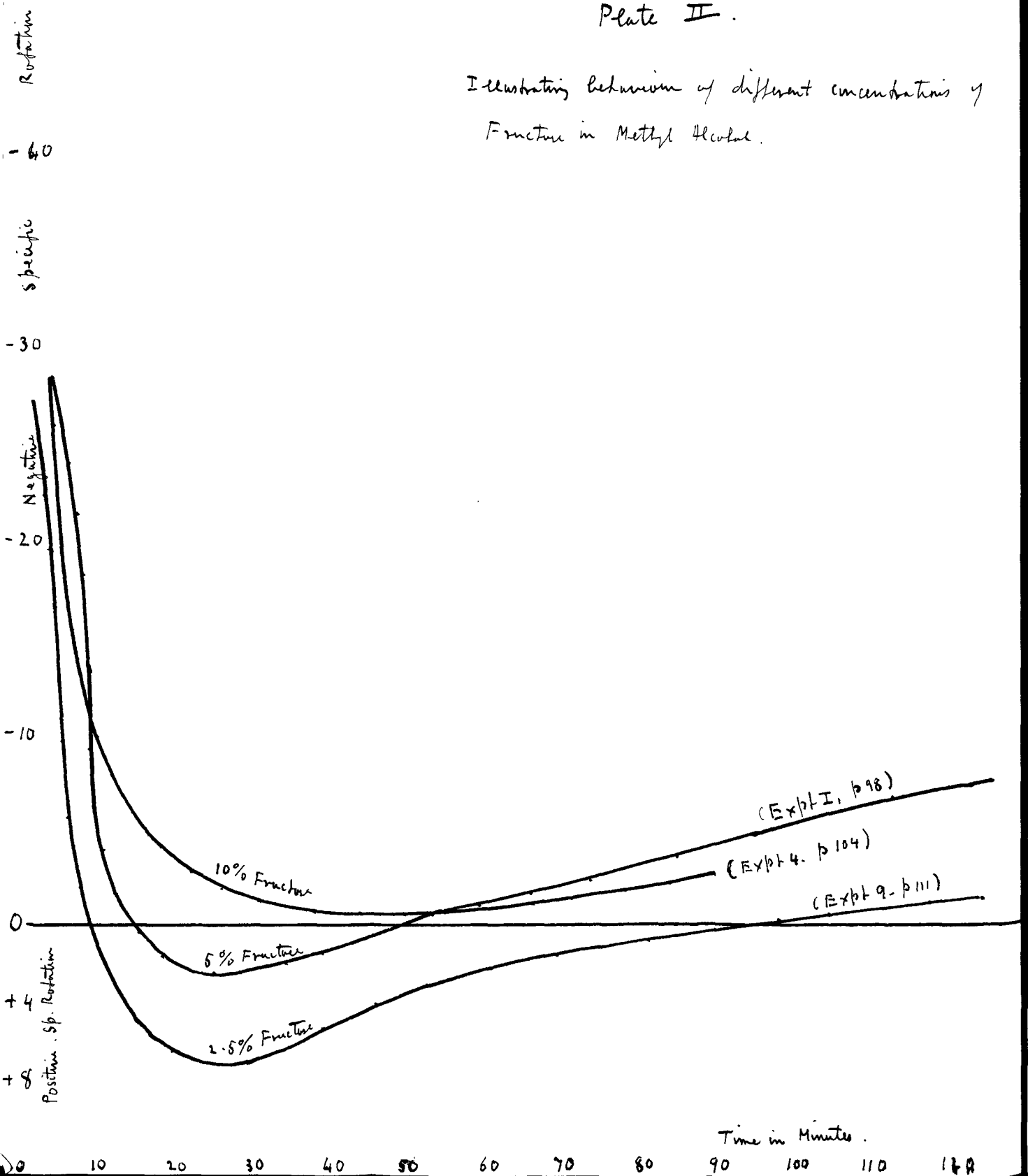
[x] It is apart from the main thread of this argument, but is nevertheless interesting to recall that thallous oxide, an alkali comparable in strength with the oxides of the alkali metals, is also soluble in alcohol, and combines with this the advantages of forming a sparingly soluble chloride, and of exerting reducing rather than oxidising effects.

Plate II.

Illustrating behaviour of different concentrations of Fructose in Methyl Alcohol.



Effect of varying concentration of Fructose.

The next series of curves shows the changes observed in fructose solutions of different strengths. It will be seen that the greatest changes in specific rotation are displayed by the weakest solutions. If the effect of water be kept in mind, and also the probability that the more fructose present the more water will be liberated, and the more unchanged fructose will remain at any stage, a sequence of ideas is obtained which afford a satisfactory explanation of the observed changes.

It will be noted that change of sign is first apparent with a 5 p.c. solution.

Plate III.

Illustrating (1) Behaviour of Methyl Alcohol recovered from a previous experiment.

(2) Effect of Acetone.

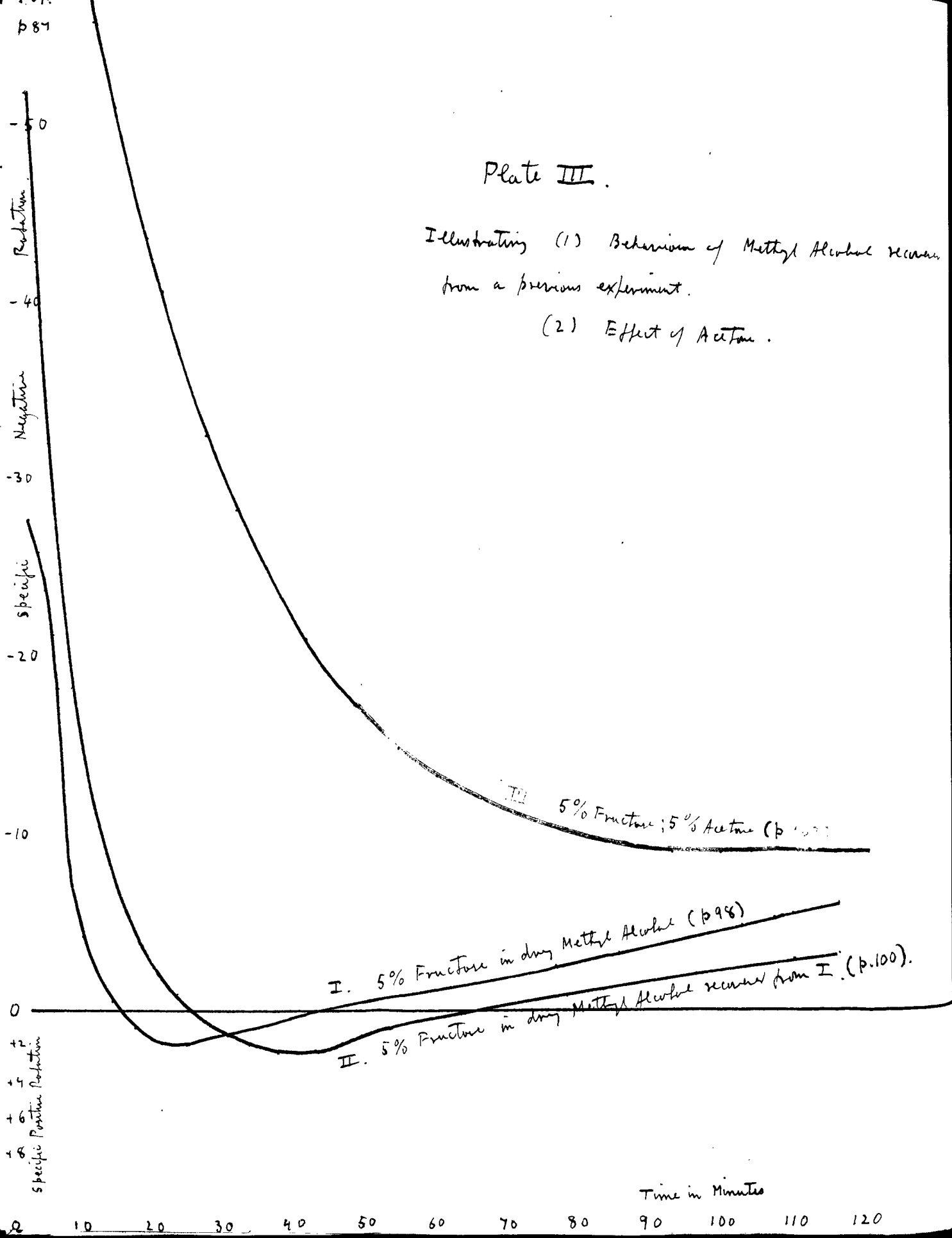
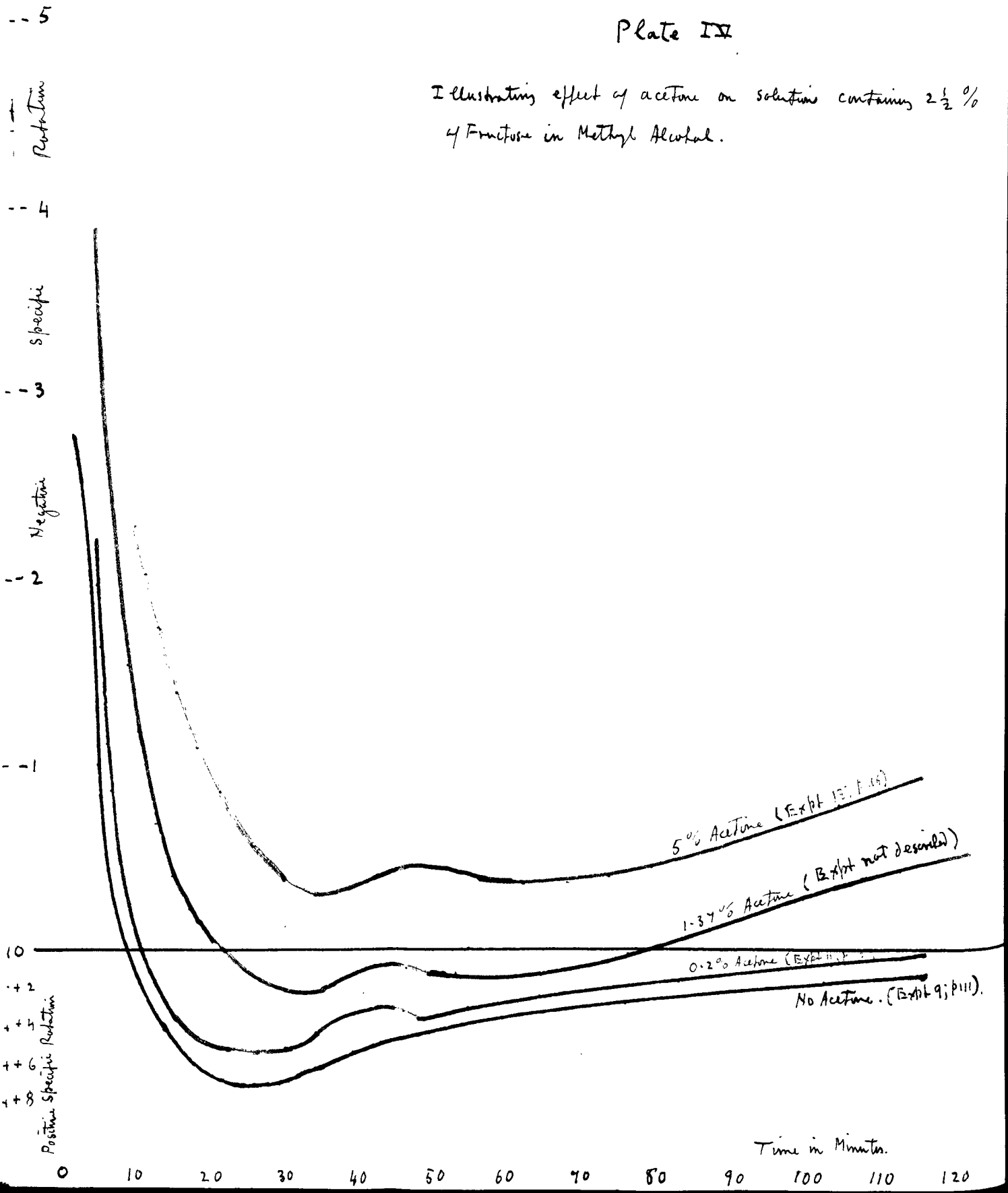


Plate IX

Illustrating effect of acetone on solutions containing 2½ % of Fructose in Methyl Alcohol.



Effects of acetone on the condensation of fructose with methyl alcohol.

The red curves in plates III and IV illustrate the effect of different percentages of acetone on the optical changes of solutions containing respectively 2½ p.c. and 5 p.c. of fructose dissolved in acidified methyl alcohol. Those optical changes are to a certain extent comparable with those produced by small quantities of water, but it will be seen that weight for weight water produces the greater effect. There can be no doubt that part, at any rate, of the effect of acetone is due to the water produced as a result of the condensation of the ketone and the sugar.

Irvine and Robertson's work affords conclusive evidence that condensation does take place, and this as already pointed out naturally also proves the formation of water.

The whole matter under discussion, however, is a complex one, and that the influence of water affords only a partial explanation is evident from the fact that all series of readings taken in presence of acetone display two maxima. This appears at once from inspection of the curves illustrating the behaviour of solutions containing 2½ p.c. of fructose. In the case

of the curve illustrating the behaviour of a solution containing 5 p.c. of fructose and 5 p.c. of acetone, the double maxima do not occur until later, but they do exist as will be seen from the figures given for the Experiment indexed in Part III as Fructose Experiment III.

It will be recalled that Irvine and Robertson working with a sugar concentration of approximately 10 p.c. of fructose obtained when the condensation was arrested at the maximum rotation:-

1 gram of methylfructosidemonoacetone from 135 cc of methyl alcohol containing 5 p.c. of acetone, or 6·75 grams of acetone in all. Now, 1 gram of methylfructosidemonoacetone requires 0·234 grams of acetone for its formation, so that on arresting the reaction at the maximum these authors retained 0·234 grams of acetone combined with fructose out of 6·75 grams originally taken. This is 3·47 p.c.

In the same way, but arresting the reaction when the rotation had increased to the maximum and again diminished to the original value, they obtained from 315 cc of the same methyl alcohol 4·3 grams of methylfructosidemonoacetone. That is to say, of 15·75 grams of acetone taken, 1 gram has been retained in combination with the fructose or 6·35 p.c.

Calculations based on the results of experiments XI to XIV show that using 2½ p.c. fructose and 0·2 of acetone,

5 p.c. of the ketone taken is retained by the fructose after 39 minutes when the maximum value of the rotation was obtained, while on allowing a similar mixture to stand for 9 days, 8·4 p.c. of the acetone originally present is utilised in the condensation.

Finally, using 2½ p.c. of fructose and methyl alcohol containing 5 p.c. of acetone, 2 p.c. of the ketone reacts with the sugar after a period of 44 minutes and 3 p.c. after three days.

As a result of the work described in Part I of this Thesis, a supply of pure methyl alcohol free from acetone was available and consequently the research was supplemented by a polarimetric study of the reaction between the alcohol and fructose. Obviously previous research on this subject has been complicated by the presence of acetone which takes part in a secondary condensation. Side reactions of this type are not limited to cases where the alcohol used admittedly contains acetone, but occur also when the so-called "acetone frei methyl alkohol" is employed, as this material may contain from 0·2 to 0·8 p.c. of the ketone.

This explains the choice of a 0·2 p.c. solution of acetone on the one hand and a 5 p.c. solution on the other, as these represent the range of purity in which methyl alcohol can be obtained by ordinary methods.

The experiments in question therefore afford comparative data for the whole range of acetone content encountered in laboratory materials.

It is evident that a solution of fructose in methyl alcohol containing 0·5 p.c. of hydrogen chloride does not function quantitatively in removing acetone which may be present in the solvent, but the results now contributed enable the whole mechanism of methylfructoside formation to be explained.

When perfectly pure methyl alcohol is used, the sugar reacts to give a dextro-rotatory methyl fructoside which has now been isolated and analysed. Despite the fact that the compound reduces potassium permanganate only slowly there can be little doubt that the fructoside is a derivative of the γ - sugar. Its instability to hydrolytic agents and its dextro-rotation are in marked contrast to the properties of β -methylfructoside as described by Hudson (J. Amer. Chem. Soc., 1916, 38, 1216) and these functions point clearly to the idea that the compound is derived from a fructose displaying a dextro rotation. To this argument has to be added the ease with which the compound enters into condensation with acetone, as although this reaction has not been studied in the case of Hudson's β -methylfructoside it is not characteristic of glucosides generally, except when they are of the γ - type.

It is consequently a reasonable explanation to claim that the first optical inversion shown by fructose dissolved in acid methyl alcohol is due to the formation of γ methylfructoside and the subsequent change in rotation results from the conversion of this form into an equilibrium mixture containing the more stable varieties of normal type. A similar explanation has been put forward by Irvine and Robertson, and it accounts fully for the earlier results obtained by Purdie and Paul, but all previous work on the subject has been greatly complicated by the presence of residual acetone in the alcohol employed.

This acetone, it has been shown, has the following effects:-

(1) The speed of fructoside formation is diminished.

(2) Condensation of the ketone with the fructoside takes place.

(3) Condensation probably takes place between the ketone and the free sugar.

(4) The solution no longer becomes dextrorotatory.

The fact that acetone continues to combine with the sugar after the maximum of the curve is formed is not inconsistent with the idea that the reaction involves a γ methylfructoside as Purdie and Paul's results show

clearly that a considerable proportion of this compound survives even after 200 hours.

It is a remarkable fact that a reaction of this nature which is of special importance in the sugar group should be affected so profoundly by the mere traces of acetone which are invariably present in the reagent necessary for the change. The idea is not fully realised that only the purest possible materials should be employed in research work on the sugars and the reactions now described may serve to emphasise this necessity.

PART III.

DETAILS OF EXPERIMENTS DISCUSSED IN PART II.

Preliminary Notes.

The experiments indexed below as Nos. 1,2. and 3 were initial experiments, and in their description the concentrations are expressed in grams per 100 cc. of methyl alcohol taken. It was afterwards found more convenient (in experiment No 4 and onwards) to express the concentration in grams per 100 cc. of solution made up.

Nos. 1, 2, and 3 were done at room temperature; the others in a jacketed polarimeter tube kept at 20°.

By an oversight, not observed in time, the experiments referred to by means of Roman numerals in part II are now referred to below by means of Arabic numerals.

Fructose Experiment No. 1. 18.2.21.

In this experiment a solution was made up containing 5.54 grams of fructose and 0.54 gram of hydrogen chloride per 100 cc. The actual quantities taken are given below.

After 2 hours 20 minutes the action was stopped by neutralisation with sodium dissolved in methyl alcohol; the whole methyl alcohol was recovered and the recovered alcohol used for experiment No, 2.

Inspection of the record of this latter

Fructose Experiment No 1 Contd.

experiment indicates that the behaviour of the recovered alcohol as regards fructose was almost identical with that of the original methyl alcohol used.

Description of Methyl Alcohol used in Experiment No.1.

This alcohol was prepared by dehydration over lime,and later over sodium, of a quantity of acetone-free alcohol purified from acetone by the hypochlorite method, but which still contained about 10% of water.

The fraction used had the following properties:-

Density $20^{o}/15^{o}$:- 0.7939. (99.5% by weight).

Boiling point 66^{o} (uncorrected).

" Acetone equivalent " 0.031%; also found 0.023%.

N,B. Densuty taken by specific gravity balance.

Using the methyl alcohol described above as solvent the following solution was made up:-

Fructose Experiment No.1 Contd.

Methyl alcohol, 250cc.) heating under reflux
Fructose. 16gms.) necessary for solution.

Hydrogen chloride N/1 (in same methyl alcohol) 44cc. (1.584 gms).

The hydrochloric acid was added rapidly after solution of the fructose and cooling of the solution. A 2 dm. tube was filled with a portion of the solution. The following readings were obtained:-

Time of adding hydrogen chloride 12.47 P.M. 18.2.21.

Time of day.	Time from zero.	Observed rotation.
12.51½.	4½.	- 2.88.
12.54.	7.	-1.84.
12.55½.	8½.	- 0.91.
12.58.	11.	-0.22.
1.1.	14.	-0.10.
1.5.	18.	+0.07.
1.8.	21.	+0.22.
1.13.	26.	+0.25.
1.17.	30.	+0.20.
1.21.	34.	+0.14.
1.30.	43.	+0.05.
1.37.	50.	+0.04.
1.45.	58.	-0.10.
1.51.	64.	-0.13.
2.14.	87.	+0.35. (- sign)
2.31.	104.	-0.56.
2.48.	121.	-0.64.
3.8.	141.	-0.76.

plotted in Plate III p.87

Fructose Experiment No, 1. Contd.

At 3.8. P.M. i.e. 2h. 18 m. from the start, the main bulk (about 280 cc.) of the solution was neutralised. The readings in the polarimeter tube, however, were continued as follows :-

Time of day.	Time from zero.	Observed rotation.
3.35 P.M. 18.2.21.	168.	-1.12.
3.57.	190.	-1.25.
4.32.	225.	-1.48.
4.55.	248.	-1.62.
5.45.	298.	-1.96.
6.30.	343.	-2.05.
10.55 A.M. 19.2.21.	1328.	-4.65.
3.P.M.	1573.	-4.91.
6.49.		-5.38.
10.40. A.M. 20.2.21.	27531.	-6.08.
12.30.P.M.		-6.2.

At this stage the contents of the polarimeter tube (about 18 cc.) were poured into a dry flask and mixed with 2cc. of acetone. The polarimeter tube was then refilled and the readings continued as below:-

12.35. P.M. 20.2.21.	-5.54.
12.38.	- 5.65.
12.45.	-5.96.
12.53.	-5.87.
12.55.	-5.7.
12.58.	-5.91.
2.7.	-6.15.

Contents of tube were now thrown out .

Neutralisation of main bulk of solution after above experiment had been in progress 2h. 18m. and recovery of methyl alcohol.

The main bulk of the solution (referred to on top of this page) was neutralised with a solution of sodium in same methyl alcohol.

Fructose Experiment No, 1, Contd.

The alcohol was now fractionated off.

1st. Fraction Volume 180 cc. Density 0.7955 18°/15°.
Boiling point 64°-66.5°.
"Acetone" .031% and .033% mean .032%.

2nd. Fraction Volume 85 cc. Density 0.7999 15°/15°.
Boiling point 66.5°- 67°.
"Acetone" .035% and .046% mean .04%.

It thus appears that the recovered alcohol has practically the same physical constants and acetone equivalent as that originally used .

Fraction No. 1 above was now used for Experiment No.2.

Fructose Experiment No. 2.

The following solution was made up:-

105 cc. methyl alcohol recovered as above;
7 grams fructose
27.6 cc. of a 2.4 solution of Hydrogen chloride in dry methyl alcohol free from acetone.

This solution consequently contains 5.16 grams of fructose and 0.5 grams of hydrogen chloride for each 100 cc. of methyl alcohol taken. The following readings were obtained in a 2 dcm. tube at room temperature.

Time of adding acid 12.32.P.M. 19.2.21.

Fructose Experiment No. 2 Contd.

Time of day.	Time from zero.	Observed rotation.
12.34 P.M. 19.2.21.	2.	-5.
12.35.	3.	-4.04.
12.36.	4.	-3.51.
12.37.	5.	-3.1.
12.39.	7.	-2.67.
12.41.	9.	-1.88.
12.43.	11.	-1.15.
12.45.	13.	-0.9.
12.47.	15.	-0.65.
12.50.	18.	-0.4.
12.54.	22.	-0.12.
1. 0.	28.	+0.05.
1.6.	34.	+0. 25.
1.12.	40.	+0.25.
1.19.	47.	+0.17.
1.22.	50.	+0.19.
1.30.	58.	+0.14.
1.37.	65.	+ 0.1.
2.14.	102. Plotted in Plate III.	-0.25.
2.57.	145. p. 87.	-0.53.
4.6.	214.	-0.85.
6.47.	373.	-1.13.
10.35 A.M. 20.2.21.	1320.	-3.1.
5.20. P.M.	1726.	-4.6.
8.35.	1921.	-4.12. (?)
10.42.	2048.	-4.04.
9.50. A.M. 21.2.21.	2718.	-4.48.

No further observations were made on this material. But inspection of these figures, and their comparisom with those obtained in experiment No.1. show that the recovered alcohol behaves similarly to that originally used. The other points arising are investigated in later experiments.

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Fructose Experiment No. 3.

In this experiment the proportions of experiment No. 2 were repeated with the difference that 5% of the alcohol was replaced with 5% of acetone .

The following solution was made up:-

22.75 cc. dry methyl alcohol free from acetone.
1.75 grams of fructose.
6.9 cc. of a 2.4% solution of hydrogen chloride
2 cc. of acetone.

These proportions correspond to 5,51 grams of fructose, 0.523 grams of hydrogen chloride and 5.06 grams of acetone per 100 cc of acetone taken.

It may be said that experiments Nos. 1,2, and 3 were preliminary experiments and were made up so as to contain approximately the percentages indicated . The rotations, moreover, were taken at room temperature. In further experiments the concentration of fructose was adjusted more accurately to the percentages stated, and by using a water jacketed polarimeter tube the temperature was kept in every case at 20° for the first few hours. Temperature control over a longer period was rendered impossible owing to the irregularities in the gas and electric supplies due to the coal strike.

To return to experiment No. 3 the following readings were obtained:-

Time of adding acid 6 P.M. 20.2.21.

Fructose Experiment No. 3. Contd.

Time of day.	Time from zero.	observed rotation.
6.3. P.M. 20.2.21.	3.	-7.1.
6.5½.	5½.	-6.66.
6.9.	9.	-5.94.
6.13.	13.	-5.2.
6.18.	18.	-4.42.
6.41½.	41½.	-2.13.
6.50.	50.	-1.68.
7.10.	70.	-1.09.
7.25.	85.	-0.94.
7.37.	97.	-0.84.
7.45.	105. Plotted in Plate III. p. 87	-0.88.
8.19.	139.	-0.89.
8.24.	144.	-0.87.
8.30.	150.	-0.86.
10.36.	276.	-1.16.
9.45 A.M. 21.2.21.	945.	-2.39.
12 noon. 22.2.21.		-5.75.

The above figures show the effect of acetone in depressing the rotation at all stages of the reaction. Attention may also be drawn to the double maxima occurring at 97 and at 150 minutes from the start. These double maxima will be shown to occur invariably in the presence of acetone, but not in its absence.

Note with regard to the solution of hydrogen chloride in dry acetone-free methyl alcohol used for all subsequent experiments.

This was made up by dissolving hydrogen chloride gas dried by passing through sulphuric acid in pure methyl alcohol. Its strength on 4/3/21 was found by titration to be 5.4%, on 21.5.21.to be 4.96%, and finally on 8.6.21 to be 4.5%% This is probably due to slow formation of

methyl chloride. As the fact that this change in acid strength was not realised to be in progress till after the experiments carried out as described below had been completed, the actual strength of hydrogen chloride present at any given date was calculated by interpolation between the above figures. It may be said that the three points obtained by plotting the above dates against the corresponding acid strengths lie almost on a straight line.

Fructose Experiment No, 4.

10% Fructose.
0.486% Hydrogen Chloride.

A 10% solution of fructose was prepared as follows:-

10 grams of fructose were dissolved in methyl alcohol under reflux. The solution was cooled and made up to 91 cc. with methyl alcohol. To this was added immediately before the polarimetric observations 9 cc. of 5.4% hydrogen chloride in methyl alcohol.

Rotations observed in 1 dm. tube.

Time of starting 12.20 P.M.

Fructose experiment No, 4. Contd.

Time of day.	Time from zero.	Observed rotation.
12.35 P.M. 6.5.21.	5.	-2.75.
12.28.	8.	-1.5.
12.30.	10.	-1.25.
12.32.	12.	-0.75.
12.34.	14.	-0.5.
12.37.	17.	-0.5.
12.40.	20.	-0.3.
12.44.	24.	-0.265.
12.46.	26.	-0.17.
12.55.	35.	-0.1.
12.56.	36.	-0.09.
12.59½.	40.	-0.08.
1.6.	46.	-0.08.
1.10.	50.	-0.14.
1.15.	55.	-0.17.
1.20.	60.	-0.16.
1.50.	90. plotted in plate II. p.85	-0.25.

(Neutralised at this point.)

It may be said that the methyl alcohol used for experiment No. 4 was acetone-free and had been dried over sodium, but wome weeks previous to its use.

The solution, carefully neutralised, by sodium dissolved in methyl alcohol was now divided into two parts A. and B.

A. the methyl alcohol was distilled off in vacuo and a 0.2% solution of hydrogen chloride in water was added to the residue, and the distillation repeated. No acetone could be found in this aqueous distillate.

B. the methyl alcohol was distilled off in vacuo and the syrup remaining was analysed :-

Found (allowing in each case for ash found in boat after combustion amounting to 6.21% of weight of dried syrup):

C = 41.89%; H = 7.41%; OMe 1) = 16.17%)
2) = 16.15%) mean 16.16%.

$C_7H_{14}O_6$ requires
C = 43.3%; H = 7.2%; OMe = 15.89%.

$C_6H_{12}O_6$ requires
C = 40%; H = 6.7%.

CH_3OH requires
C = 37.5%; H = 12.5%.

Details of above analyses.

12.521. Estimation of methoxy group by Zeisel's method.

Fructose Experiment No. 4. Contd.

Zeisel on Syrup B.

Weight taken 0.2077 grams.
weight after drying 0.2064 grams.
Weight of silver iodide obtained 0.2371 grams.
Weight after further drying 0.2366 grams.

These figures give 15.17% OMe in total syrup and 16.17% in syrup less ash found on combustion.

9.6.21. In view of the possibility that the drying of the syrup in preparation for the above analysis might have been incomplete, the methoxy content found being slightly above the theoretical, the Zeisel was repeated. It may be noted that the syrup was found to be acid at this date on testing it with litmus.

Details of second Zeisel on above syrup.

(1). Weight of undried syrup 0.4865 grams.
(2). After 6 hours at 60°/ 760mm, 0.4373 grams.
(3). After 16 hours at 60°/160to 60 mm. 0.4044 grams.
(4). After 2 hours at 60°/ 10 mm. 0.4046 gram.
(5). Weight of silver iodide obtained by Zeisel 0.4643 gram.

These figures give 15.15% OMe in total syrup or 16.15% allowing for ash, a figure agreeing with the previous one within the limits of experimental error.

Combustion on Syrup B. 13.5.21.

(1). Weight taken 0.5336.
(2). 4 hours at 65°/ 160 mm. 0.3166 gram.
(3). 2 hours at 65°/ 160 mm. 0.3160 gram.
(4). Weight of ash in boat after combustion 0.196 gram. or 6.21% of weight of dried syrup. This ash contained 46% of chlorine as against 60.7% required by NaCl
(5). Weight of water formed on combustion 0.1962 gram.
(6). Weight of carbon dioxide 0.4551 gram.

These figures give, allowing for the ash, C 41.89% H 7.41% .

Fructose Experiment No. 4 Contd.

There is no reason to suspect the results of this analysis. The figures obtained compared with those required by methyl fructoside, fructose, and methyl alcohol are consistant with the idea that all three substances are present, and it will be seen from the figures given concerning the loss of weight of a similar syrup in experiment No. 5 that drying in vacuo at a temperature of 75° results in further loss of weight.

Fructose Experiment No. 5.

2½% Fructose 0.5% Hydrogen chloride.

This solution was made up 10.5.21. the acid being added at 7.35 P.M. The rotations were taken in a jacketed tube (2 dm.) at 20°.

Time of day.	Time from zero.	Observed rotation.
4.1. P.M. 10.5.21.	4.	-0.98.
4.4	7.	-0.37.
4.6½.	9½.	-0.12.
4.12.	15.	+0.1.
4.18.	21.	+0.15.
4.23.	26.	+0.15.
4.28.	31.	+0.14.
4.37.	40.	+0.14.

The solution was then neutralised and allowed to evaporate slowly in a vacuum dessicator over sulphuric acid. Since the previous syrup isolated (experiment No, 4) was found to be slightly acid care was taken to keep the present one faintly alkaline.

7.6.21. The syrup had by this time evaporated down to small bulk and had deposited cubical crystals resembling those of sodium chloride. The syrup was consequently dissolved in sufficient methyl alcohol to enable it to be filtered from the crystals. The filtered liquid was evaporated down in vacuo at about 50° and on a portion of this a Zeisel was done as described below.

Fructose Experiment No. 5 Contd.

9.6.21. Another portion of the syrup, (0.9 gram partially dried; as shown in figures for Zeisel below part of the same sample lost 20% of its weight on careful drying, so that this 0.9 gram contained 0.72 gram of dry syrup), was dissolved in 20 cc of dry acetone-free methyl alcohol and rotations were taken at room temperature. Visibility was low in spite of a good sodium flame, and the readings obtained:-
+0.15, +0.08, +0.16, +0.04, mean +0.11.
were not in close agreement, but all were positive.
While no exact figure for the specific rotation of this substance can be deduced from the above rough experiment it is obvious that it was definitely dextrorotatory.
It may be said that this syrup had been kept faintly alkaline to litmus throughout.

Details of Zeisel on above syrup.

(1). Weight taken 0.5353.
(2). After 4 hours 60°/760 mm in dry air 0.4574 gram.
(3). After 16 hours 50-60°/ 160-60 mm 0.4174 gram.
(4). After 1 hour 60-70°/ 10 mm 0.4152 gram.
(5). After 1 hour more 50-60°/ 10 mm. 0.4150 gram.
(6). Weight of silver iodide by Zeisel's method 0.4659 gram

This gives OMe = 14.82% of total syrup or allowing for ash (7%) OMe =15.94% .
The theory as already shown requires 15.89% .
Owing to a slight loss in manipulation this result is a little low.

Combustion on above syrup.

(1). Weight taken, 0.4939. gram
(2). 4 hours; 10 mm; room temperature 0.4176 gram.
(3). 1½ hours; 10 mm; 50-65° 0.3927 gram.
(4). 1½ hours; 10 mm; 50-60° 0.3903 gram.
(5). 2 hours; 10 mm; 70-75° 0.3836 gram.
(6). 1½ hours; 10 mm; 50-60° weight unchanged.
(7). Weight of ash after combustion 0.0268 gram, or 6.99% of weight of dried syrup. This ash contained 44.6% of chlorine as against 60.7% required by NaCl.
(8). Water formed by combustion 0.2393 gram.
(9). Weight of carbon dioxide 0.5602 gram.

These figures indicate, allowing for the ash, C = 42.83% H = 7.2%.

Inspection of the results quoted for experiments Nos. 4 and 5 show that there can be little doubt of the formation of a dextrorotatory methylfructoside in the latter case .

Fructose Experiment No, 6.

In this and in the two following experiments, Nos. 7 and 8 the alcohol used had a density of 0.8008 at room temperature. this corresponds with approximately 1.36 grams of water in 100 cc.

For experiment no. 6 were taken :-

1.25 grams fructose.
2 cc. water.
5 cc. acid solution, already described.

The fructose was first dissolved in about 40 cc of the above methyl alcohol, 2 cc water, and 5 cc. acid solution were then added and the solution made up to 50 cc. with pure methyl alcohol. Readings taken in 2 dm. jacketed tube at 20° .
Time of mixing 11.51 P.M. 23.5.21.

Time of day.	Time from zero.	Observed rotation.
11.54.	3,	-3.2.
11.56.	5.	-2.92.
12.1.	10.	-2.54.
12.5.	14.	-2.59.
12.10.	19.	-2.42.
12.16.	25.	-2.28.
12.21.	30.	-2.14.
12.30.	39.	-2.03.
12.40.	49.	-1.81.
12.50.	59.	-1.68.
1.0.	69.	-.1.46.
1.10.	79.	-1.54.
1.12.	81.	-1.46.
2.4.	133. Plotted on Plate I. p. 82	-1.09.

The quantities taken above are equivalent to 2½ grams of fructose, and 5.36 grams of water per 100 cc.
No acetone was present.

Fructose Experiment No. 7. 23.5.21.

Solution made up to contain $2\frac{1}{2}$ grams fructose, 0.491 grams hydrogen chloride, 1.36 grams of water, in 100cc. (water estimated by density as already explained).

No acetone was present.

Actually taken 0.6250 grams fructose, 2.5 cc acid of strength 4.91% (by interpolation as already explained)

Done in 2 dm. tube at 20°. Mixed 5.56 P.M.

Time of day.	Time from zero.	Observed rotation.
5.59. 23.5.21.	3.	-2.4.
6.$2\frac{1}{2}$.	$6\frac{1}{2}$.	-1.45.
6.6.	10.	-1.06.
6.13.	17.	-.0.59.
6.17.	21.	-0.25.
6.$22\frac{1}{2}$.	$26\frac{1}{2}$.	-0.18.
6.36.	30. Not plotted	-0.12.

Gas turned off at main at 6,30 P.M. owing to coal shortage.

Fructose Experiment No, 8. 24.5.21.

Repeat of above. But acid being one day older was now 4.88%.

Time of day.	Time from zero.	Observed rotation,
9.58. A.M.	0.	-
10.0$\frac{1}{2}$.	$2\frac{1}{2}$.	-2.5.
10.2.	4.	-2.16.
10.4.	6.	-1.72.
10.7.	9.	-1.34.
10.11.	13.	-0.9.
10.20.	22.	-0.2.
10.31$\frac{1}{2}$.	$33\frac{1}{2}$.	-0.14.
10.37$\frac{1}{2}$.	$39\frac{1}{2}$.	-0.08.
10.48.	50.	-0.06.
10.55.	57.	-0.05.
11.4.	66.	-0.06.
11.32.	94.	-0.13.
11.57.	119.	-0.25.
12.55.	177.	-0.43.
2.45.	287 Not plotted.	-0.75.

Fructose Experiment No. 9.

2½ grams fructose, per 100 cc
0.488 gram acid per 100 cc
No water nor acetone.

The alcohol used for this and all subsequent experiments was prepared by drying that used for the three preceding experiments by distillation over sodium. Boiling point 65.2/ 765.5 mm. (on 23.5.21.) and 65.2/760.4 (on 24,5.21.).

0.6249 gram of fructose ~~being~~ were made up to 25 cc. in the usual way. Done at 20° in 2 dm. tube.

Time of day.	Time from zero.	Observed rotation.
4.54 P.M. 24.5.21.	0.	-
5.0.	6.	-0.44.
4.56.	2.	-1.39.
5.3.	9.	+0.01.
5.6.	12.	+0.16.
5.9.	15.	+0.22.
5.12½.	18½.	+0.31.
5.18½.	24½.	+0.37.
5.23.	29.	+0.33.
5.24½.	30½.	+0.26.
5.30.	36.	+0.30.
5.36½.	42½.	+0.23.
5.48.	54.	+0.21.
5.58½.	64½. Plotted on Plate I, II, & III.	+0.17.

Gas turned off at 6 P.M. owing to coal shortage.

9.30. A.M. 25.5.21.	996.	-1.32.

Fructose Experiment No. 10. 26.5.21.

2½ grams fructose. per 100 cc
1 gram water. Per 100 cc
0.484 gram acid, per 100 cc.
0.75 grams fructose made up to 30 cc.

Done in 2 dm. tube at 20°.

Time of day.	Time from zero.	Observed rotation.
3.12. P.M. 26.5.21.	0	-
3.17½.	5½	-1.75.
3.21.	9.	-1.29.
3.25½.	13½.	-0.91.
3.31.	19.	-0,59.
3.40.	28.	-0.32.
3.45½.	33½.	-0.21.
3.52.	40.	-0.10.
3.59.	47.	-0.10.
4.14½.	62½. Plotted on Plate I. p82	-0.07.
5.22.	130.	-0.18.
		light very bad.
9.10. A.M. 27.5.21.		-1.68.
9.30. A.M. 3.6.21.		-3.75.

Fructose Experiment No. 11.

2.5 grams fructose.
0.486 grams acid.
0.2 grams acetone, per 100 cc in each case.
0.6252 grams fructose made up to 25 cc.

Done in 2 dm. tube 20°.

Time of day.	Time from zero.	Observed rotation.
3.45 P.M. 25.5.21.	0.	-
3.49.	4.	-1.04.
3.50½.	5½.	-0.53.
3.53.	8.	-0.20.
3.55½.	10½.	+0.06.
3.59.	14.	+0.17.
4.2.	17.	+0.30.
4.5½.	20½.	+0.20.
4.8½.	23½.	+0.25.
4.13.	28.	+0.27.
4.17½.	32½.	+0.24.
4.25½.	40½.	+0.14.
4.32.	47.	+0.18.

Fructose Experiment No 11 Contd.

Time of day.	Time from zero.	Observed rotation.
4.37.	52.	+ 0.14.
4.46.	61.	+0.12.
4.53.	68.	+ 0.10.
9.0 A.M. 26.5.21.		-1.83.
10.0 A.M. 3.6.21.		-3.3.

plotted on Plate III. p.88

On this last day (3.6.21.) the liquid in the tube (16.5 cc) was neutralised with 4 cc. of a solution of sodium in dry methyl alcohol, this being sufficient to render the liquid very faintly alkaline to litmus. The neutralised liquid (20.5 cc.) was then placed in a small flask and the methyl alcohol distilled off by immersing the flask in boiling water. This distillate (referred to below as " Distillate A") naturally also contained such acetone as had not combined with the fructose. This first distillation took 15-20 minutes, after which time 18 cc. had distilled off. The flask was then evacuated for 3 minutes, still being immersed in hot water. After this 5 cc. of normal sulphuric acid and 20 cc. of water were added, and about half of this was distilled off ("Distillate B").

As compounds of the sugars with acetone are very readily hydrolysed by acids, distillate B. must have contained all acetone present in combination with the fructose and methylfructoside before acidification.

It is now required to estimate 1) acetone originally present in the 16.5 cc. of solution in the polarimeter tube. 2) Acetone in distillate A, and 3) that in distillate B.

1) Acetone originally present. This was 0.2% of 16.5 cc., or 0.033 grams.

2) Acetone in distillate A. On applying Messenger's test to the whole distillate 13.9 cc. N/5 Iodine were required. 1 cc. N/5 Iodine corresponds to .001933 gram of acetone, consequently distillate A. contains .0267 gram of acetone this being 80% of the acetone originally taken.

3) Acetone in distillate B. This required 1.43 cc. N/5 Iodine and consequently contained .00276 gram of acetone this being 8.4% of that taken .

It thus appears that in a solution containing 0.2 gram acetone, 2.5 grams fructose and 0.5 gram hydrogen chloride made up to 100 cc. with pure dry methyl alcohol,

Fructose Experiment No. 11 Contd.

after eight days only 8.4% of the acetone combined with the fructose in a form stable in neutral or faintly alkaline solution, but decomposed by acids.

In this case 88.4% of the acetone taken has been accounted for.

The above experiment and the three final experiments Nos.12. 13. and 14 are all concerned with the amount of acetone retained by fructose dissolved in methyl alcohol (2½ grams in 100 cc. in each case) after different periods of time. The same procedure was followed in each case, and as this has been explained fully above more condensed descriptions are given below. In each case "Distillate A" indicates the alcoholic distillate containing acetone not retained by fructose, while " Distillate B" indicates the aqueous distillate obtained after acidification of the residue and therefore containing acetone previously retained by fructose.

It will be observed that in no case is all the acetone taken accounted for, and that this deficiency increases with increased concentration of acetone. Both points are in keeping with the well known tendancy of acetone to condense with itself with formation of compounds of high boiling points.

Fructose Experiment No.12. 3.6.21.

2.5 grams of fructose.
0.462 gram. hydrogen chloride.
0.2 gram acetone, per 100 cc.

This experiment is a repetition of No,11 with the difference that the reaction was stopped after 40 minutes near the maximum positive rotation. The experiment was done in a 2 dm. tube at 20°.

The following readings were obtained:-

Time of day.	Time from zero.	Observed rotation.
12.13.	0.	-
12.17.	4,	-1.05.
12.22.	9.	-.0.28.
12.24.	11.	-0.15.
12.33.	20.	+0.20.
12.35.	22.	+0.24.
12.39.	26.	+0.23.
12.42.	29.	+0.23.
12.45.	32.	+0.30.
12.50.	37.	+0.25.
12.52.	39. Not plotted	+0.22.

At this stage the whole bulk of liquid was neutralised . 30 cc. of solution were originally made up, but owing to loss in filling and emptying the polarimeter tube distillations were performed on 28.5 cc. It may be added that the solution not in the tube was also kept in a flask immersed in water at 20° during the readings. The examination of the distribution the acetone was conducted as already described under experiment No, 11.

1) Acetone originally present. This was 0.2% of 28.5 cc. or 0.057 gram .

2) Acetone in alcoholic distillate A. (i.e. Not combined with fructose) This required 25.6 cc. N/5 Iodine, and consequently amounted to 0.495 gram, or 87% of the acetone taken .

3) Acetone in aqueous distillate B. (i.e. combined with fructose) The total distillate required 1.45 cc. N/5 Iodine, and thus contained .0028 gram. of acetone, or 4.9% of that taken.

Fructose Experiment No 12 Contd.

In this case 91.9% of the acetone taken has been taken.

The results of experiments Nos 11, and 12 show that the amount of acetone taken into combination by the sugar in 40 minutes after acidification is more than half of that taken up after 8 days .

Experiment No. 13. 6.6.21.

$2\frac{1}{2}$ grams Fructose. Per 100 cc.
0.457 grams Hydrogen chloride. Per 100 cc
5 grams Acetone per 100 cc.
0.7500 gram Fructose per 30 cc.

Done in 2 dm. tube at 20° .

Time of day.	Time from zero.	Observed rotation.
12.30.	9.	-1.15.
12.35.	14.	-0.72.
12.38½.	17½.	-0.43.
12.44.	23.	-0.33.
12.48.	27.	-0.14.
12.53½.	32½.	-0.14.
12.58½.	37½.	-0.16.
1.5.	44. Plotted on Plate IV. p 88	-0.33.

The readings in the tube were continued as given below in Experiment No. 14. At this stage the liquid remaining in the flask (also kept at 20°) was neutralised, and examined for acetone as before. Its volume was 11.5 cc.

1) Acetone originally present . This was 5% of 11.5 cc. or 0.575 gram.

2) Acetone in alcoholic distillate A. The total of this distillate was 18.7 cc. (the increase from 11.5 cc. being due to alcohol added as solvent for sodium methoxide used for neutralisation). This distillate contained 3.36 grams of acetone per 100 cc. or 0.46 gram in all; this is 80% of the acetone taken.

Fructose Experiment No. 13 Contd.

3) Acetone in aqueous distillate B. This corresponded to 6.3 cc. N/5 Iodine and thus contained 0.0122 gram of acetone, or 2.1% of that taken.

In this experiment 83.6% of the acetone taken has been accounted for.

Fructose Experiment No. 14.

Same solution as used in experiment No.13. for polarimetric readings, which were continued as given below:-

Time of day.		Time from zero.	Observed rotation.
12.21. P.M.	6.6.21.	0	-
1.22.		61.	-0.17.
2.33.		132.	-0.59.
3.26.		185.	-0.95.
8. 0 P.M.	8.6.21.	8	-3.67.
12 noon.	9.6.21.		-3.86.

The solution was then poured into a flask, neutralised, and examined as before, total volume 17 cc.

1) Acetone originally present. 5% in 17 cc. or 0.85 gram.

2) Acetone in alcoholic distillate A. Volume 19 cc. Found by Messenger's method to contain 3.14% of acetone or 0.596 gram in all, this is 70% of that taken.

3) Acetone in aqueous distillate B. The whole distillate required 13.9 cc. N/5 Iodine, and thus contained 0.27 gram, or 3.2% of the acetone originally taken .

In this experiment only 73.2% of the acetone taken has been accounted for. As already indicated this is probably due to the tendency of the ketone to condense with itself.

Inspection of the results of the last four experiments show that the most rapid condensation between acetone and fructose dissolved in methyl alcohol occurs during the period immediately after acidification.

It is during this initial period also that the rapid changes in sign take place and during which the formation of a dextrorotatary methyl fructoside has now been established.

The probable connection between these results has been discussed towards the end of Part II.

In conclusion the writer wishes to acknowledge his indebtedness to Principal Irvine for the sympathetic interest he has taken in this work and for his advice. The writer also wishes to thank Mr. J. W. Armit M. A. for assistance in part of the experimental work.